COMPUTER MODELLING

OF THE CHEMICAL SPECIATION

IN SEAWATER

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by

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To My Parents

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ABSTRACT

The primary aim of this thesis is to establish a computer model of the chemical elements in seawater and to use this model to gain insight into the chemical processes controlling dissolution, precipitation, redox levels and coordinative interactions in surface seawater. In order to accomplish this task a relatively extensive database consisting of about 580 complexation equilibria arising from 32 inorganic and 10 organic components has been set up. Constants have been selected from critical compilations. Included in these equilibria are solubility products for the formation of potential solids, redox reactions and interactions with the atmospheric gases carbon dioxide and oxygen.

The model was validated, for the purposes of this study, by comparing computed pH values and metal speciation patterns from the modelling results with experimentally determined values from the literature. Several kinetic factors are taken into account by the model. These include kinetic considerations for the precipitation of calcite, aragonite, dolomite and magnesite under seawater conditions as well as the distribution of redox elements amongst their oxidation states by the oxygen-water or oxygen-peroxide couple. The dispute over which of the aforementioned couples is responsible for setting the redox level of surface seawater has been investigated. Of the redox elements considered in this study, namely copper, manganese and iron, manganese appeared to be the most sensitive to changes in the overall redox potential. The modelling results for the speciation of manganese at the redox level set by the oxygen-peroxide couple were found to agree well with experimentally determined speciation results reported in the literature. Assuming that manganese is a suitable indicator of redox potential, it is proposed that the reduction of oxygen to peroxide is responsible for setting the redox level of surface seawaters. The

formation of ternary mixed ligand complexes and polynuclear species has also been investigated. Results of this study show both species to be insignificant in the speciation of the metals considered. An important aspect of this thesis is an investigation into the effect of metal-fulvic acid complexation on the inorganic speciation pattern of trace metals. The approach used in this study differs from that of other workers in that the choice of model organic ligands was based on an experimental analysis of a marine fulvic acid sample, the latter being used as input to the computer program RANDOM which generates a model fulvic acid structure in terms of metal binding sites (or ligands). Analysis of modelling results showed organic metal binding to be of significance in the speciation of copper(II) at levels characteristic of surface seawaters, and of significance in the speciation of manganese(II), zinc(II), lead(II) and iron(II) at higher levels characteristic of sediments. In general however most of the organic ligands are complexed by the metals calcium and magnesium as a result of the comparitively high concentrations of these metals in seawater.

Owing to the poor agreement amongst values published in the literature for the formation constants of carbonic acid, it was decided to determine the protonation constants, and time permitting some of the formation constants for this system. The protonation constants were successfully determined in sodium perchlorate or sodium chloride using glass electrode potentiometry. The determinations of the formation constants for the copper carbonate and zinc carbonate systems were however not as successful.

The computed speciation patterns were compared with experimentally determined speciations reported in the literature. Favourable agreement between the two gave some confidence to the success of the model.

LIST OF SYMBOLS

A	Debye Hückel constant, equa. 2.3
a	activity, defined in section A2
å	stoichiometric coefficient of component i in complex j, equa.2.3
B	Debye Hückel constant, equa. 2.3
β_{pqr}	overall stoichiometric formation constant, equa. A1
C	empirical constant, equa. 2.3
E_{const}	sum of constant potentials in the electrode equa.,section A2
E_{cell}	measured emf of the cell in volts, section A2
E_h	reversible redox potential of the solution, equa. 2.6
ΔG_m^{θ}	standard molar Gibb's free energy of reaction, section 2.1
c_i	activity coefficient of the i^{th} ion, section A2
H_T	Total proton concentration, section A2
ΔH_m^{θ}	standard molar enthalpy of reaction, equa.2.2
K	stepwise formation constant,section A2
K_1, K_2	ionization constants for carbonic acid, section A1
K'	conditional constant, section 2.3.2.5
L_T	total ligand concentration, section A2
M_T	total metal concentration, section A2
pH(S)	pH assigned to a standard buffer solution, section 2.4.1.1
pH(X)	pH of test solution, section 2.4.1.1
Q	quotient of activity coefficients, section A2
γ	molar activity coefficient of an ion
S	Nernstian slope, section A2
X_j	concentration of the complex j, section 2.2.5
Y_j	difference function of component concentrations, equa. 2.10

Z_H, Z_M formation functions, section A2

‰ grams per kilogram of seawater

Abbreviations for the organic ligands used in the model

ACAC : acetylacetone

2ACPH : 2-acetylphenol

BENZ : benzoic acid

3HBA : 3-hydroxybutyric acid

2HMP : 2-hydroxy-2-methylpropanoic acid

PROP : propanoic acid

PHEN : phenol

SUCC : succinic acid

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CHAPTER ONE
GENERAL INTRODUCTION

1.1 SEAWATER

The world ocean is an enormous flywheel that controls the climate, regulates the amount of carbon dioxide, oxygen and other gases in the atmosphere, transports sediments as part of the major geological cycle, acts as a major reservoir of non-renewable resources and provides a significant portion of the food for terrestrial life forms [1]. The survival of all species is dependent upon protection of the environment and efficient management of natural resources. An ocean that is affected adversely in its important functions limits the Earth's capacity to sustain life.

The effect of man's activities on the world ocean has become a matter of great concern. The belief that the ocean is inexhaustible in all its resources, including the extent to which it receives the wastes of man, is now being challenged by a growing body of evidence that not only the surface ocean and coastal areas, but also the deep ocean are showing signs of stress [1].

In order to assess the impact of man's activities on the world ocean, and to predict the consequences of disturbances on the vast network of processes involved, a thorough understanding of the processes themselves is required. First, it is necessary to characterise the ocean in relation to the other reservoirs with which it is continuously interacting, namely the air, sediments and igneous rock. Seawater is a multicomponent electrolyte solution, the composition of which has remained more or less constant for the last few hundred million years [2]. In 1933 Goldschmidt [2] attempted to establish a geochemical balance to show how the ocean was formed by a reaction of primary igneous rock with volatiles according to the equation:

igneous rock + volatiles = seawater + air + sediments

For each litre of present-day seawater, 0.6 kg of igneous rock reacted with 1 kg of volatiles forming, in addition, 0.6 kg of sediments and 3 litres of air. Characterization of the chemical composition of seawater requires not only a knowledge of the major and minor constituents and their total concentrations, but more importantly it requires an identification of the speciation of each constituent. For our purposes the chemical speciation of a given element is defined as the identity and concentration of the individual physico-chemical forms in which that element occurs.

Metal ions in the ocean play vital roles for marine biota as either essential nutrients or toxins. The bioavailability or biotoxicity of these metals however is not determined solely by their total concentration but more important by their speciation [3, 4, 5, 6]. Numerous laboratory culture experiments with phytoplankton under seawater conditions have demonstrated that the chelation of most metals lowers their availability or toxicity to phytoplankton, presumably by lowering the concentration of the free metal ion [7]. The repression of toxicity by complexing agents has been demonstrated quantitatively in phytoplankton cultures using well characterised artificial chelating agents and copper as the toxicant [8, 9]. Both sets of results showed that growth rate inhibition and copper content of cells was related to the free ion activity and not to the total copper concentration. There is also apparent evidence for the repression of copper toxicity by complexing organic compounds released by phytoplankton and algae [10]. Although the idea of cells being able to "condition" their external environment themselves is appealing, the authors felt that the results were not conclusive and the question remains open.

The bioavailability of essential nutrients has also been shown to be affected by the presence of external chelators. For example, manganese, calcium and zinc deficiencies have been induced by the addition of the chelator EDTA to growth media [9].

The examples given above have all attributed toxicity or bioavailability to be controlled by the free metal ion. Recent studies by Magnuson *et al.* [5] on the toxicity of copper to Daphnia magna, based on data of Andrew, Biesinger and Glass, tentatively suggested that the free copper and/or the neutral and/or the cationic hydroxo complex were responsible for only 60 to 70 percent of the toxicity. The anionic hydroxo copper complexes contributed 15 to 18 percent of the toxicity and the carbonato copper complexes were non-toxic.

A thorough knowledge of the chemical speciation of elements in seawater would appear to be imperative to an understanding of the complex chemical processes occurring in the ocean. Experimental techniques can be used to determine reliably the speciation of a single-metal single-ligand system.

For the determination of speciation in a multicomponent system such as seawater however the results are much less satisfactory. In the latter case several problems are encountered:

1. Trace elements in seawater are present at very low total concentrations, typically 10^{-11} to 10^{-8} mol dm^{-3}. Only recently have reliable measurements of these *total* concentrations been made.

2. The concentrations of the large variety of complexes formed from these components are thus even lower. By and large, the task of separating these complexes and determining their concentrations exceeds the capabilities of modern analytical methods.

3. Most techniques available to date produce disturbances or perturbations of the equilibrium they are trying to measure.

Certain experimental techniques have been developed which provide some type of discrimination between the different chemical forms of trace element complexes. Anodic stripping voltametry, ion exchange chromatography, ultrafiltration, dialysis and bioassay are analytical techniques most widely used. In general however, the relationship between analytical response and chemical speciation is not well established and at best, these techniques divide species into "boxes" based on measurements which are operational rather than definitive.

One of the most powerful tools in the study of speciation in a multi-component, multiphase system such as seawater is computer modelling whereby the real system can be characterised by analogy with a simplified model system [11]. According to Nordstrom *et al.* [12] a computer model can be defined as a theoretical construct which allows one to predict the thermodynamic properties of electrolyte solutions.

1.2 MODELLING

The first attempt at characterising the chemistry of the ocean by modelling was made by Lars Gunnar Sillén in 1961 [13], in which he compared the real sea-air-sediment system with a model system at equilibrium. Obviously, since the sea is an open, dynamic system with variable inputs and outputs of energy, and since much of the chemistry of the ocean depends on the kinetics of various physical and chemical processes, as well as on biochemical reactions, rather than on equilibrium conditions, the state of equilibrium is merely a construct. The equilibrium model does, however, provide a plausible first approximation to the real system, since in all circumstances equilibrium calculations provide boundary conditions towards which the real system must be proceeding, however slowly [14].

Sillén believed that the use of a geochemical balance such as that proposed by Goldschmidt, to account for the concentrations of the major ions and the pH of seawater left too much to chance. Instead he proposed that both the pH and the main ionic concentrations were determined by heterogeneous equilibrium with the alumino-silicates. The concept of a heterogeneous equilibrium control mechanism could account for the near perfect balance of acids and bases giving rise to a pH of 8.2, as well as the constancy of the ocean composition. This proposal was contradictory to the opinion of the time, that the pH of the ocean was buffered by the carbonate equilibria.

His initial model consisted of 5 components - HCl, H_2O, SiO_2, $Al(OH)_3$, KOH, the first two representative of volatiles and the latter three representative of oxides of igneous rock. When mixed in ratios representative of those found in the real system, these give rise to three stable solid phases SiO_2 (quartz), $Al_2Si_2O_5(OH)_4$ (kaolinite) and $KA1_3Si_3O_{10}$ (K-mica) together with a gas phase and an aqueous solution of H^+, K^+ and Cl^-.

To illustrate how the alumino-silicates could regulate the pH and solution composition he considered the following reaction:

$$1.5\ Al_2\ Si_2\ O_5\ (OH)_4\ (s) + K^+ = KAl_3Si_3O_{10}(OH)_2\ (s) + 1.5\ H_2O + H^+$$

for which the equilibrium condition

$$K = [H^+]/[K^+] \qquad (1)$$

and the charge balance

$$[K^+] + [H^+] = [Cl^-] + K_w/[H^+] \qquad (2)$$

can be written. Since the constants K_w and K are determined by temperature, if the $[Cl^-]$ is fixed, both $[K^+]$ and $[H^+]$ are also fixed, and upon addition of arbitrary amounts of HCl or KOH the system will return to its original equilibrium condition provided no phase disappears completely. Hence the system is a pH-stat rather than a buffer. Interestingly enough, experiments by Julian Hemley [2] on aluminosilicate phases in equilibrium with an aqueous solution of known composition, have found a value for K defined by equation (1), of $10^{-6.0}$ and $10^{-6.5}$, whereas the actual $[H^+]/[K^+]$ ratio in seawater is about $10^{-6.2}$.

Current models of the physical chemistry of seawater, such as that of McDuff and Morel [15] and Whitfield and Turner [16] propose that the concentrations of most major elements in seawater are fixed by a dynamic balance between input and removal processes resulting in a steady-state condition, rather than by the heterogeneous equilibrium control mechanism proposed by Sillén. The model proposed by McDuff and Morel is, however, in agreement with that of Sillén, regarding the control of the acid-base chemistry (pH and alkalinity) by

heterogeneous equilibrium processes. Owing to their scepticism over the existence of sufficient quantities of authigenic silicate phases however, they propose that the regulating equilibrium is calcium carbonate deposition:

$$Ca^{2+} + 2HCO_3^- = CaCO_3(s) + CO_2(g) + H_2O$$

In order to balance the return flux of CO_2 to the atmosphere, metamorphic reactions of carbonate rock into silicate rock need also be considered:

$$CaCO_3(s) + SiO_2(s) = CaSiO_3(s) + CO_2(g)$$

The first model to describe quantitatively the chemical speciation of the major-ion constituents in seawater was proposed by Garrels and Thompson in 1962 [17]. Based on the Bjerrum ion association theory [40], the model makes use of thermodynamic dissociation constants for complexes formed from the eight major-ion species in seawater (K, Na, Ca, Mg, HCO_3^-, CO_3^{2-}, SO_4^{2-}) in conjunction with estimated values for single ion activity coefficients and mass balance equations for the ions, to obtain the concentrations of all ionic species relevant to seawater at 25°C and one atmosphere pressure. Owing to the complexity of the electrolyte medium and the fact that calculations were made without the aid of a computer, several simplifying assumptions had to be made:

1. Chloride was assumed not to form ion pairs with the medium cations.

2. Free ion activity coefficients were calculated according to the MacInnes mean salt method and were assumed to be functions of the total ionic strength only.

3. Activity coefficients of the charged ion pairs were set equal to the activity coefficient of the bicarbonate anion.

4. Activity coefficients of neutral ion pairs were set equal to that of carbonic acid.

A better understanding of ocean chemistry has led to the questioning of these assumptions. Recently, Johnson and Pytkowicz [18] gave evidence of chloride ion pairing with major cations in seawater. According to these authors, such ion pairing reduces the ionic strength of seawater from the commonly used value of 0.69 mol dm^{-3}, to a value of 0.53 mol dm^{-3} [19]. The validity of the MacInnes convention has also been questioned, since various independent calculations of single ion activity coefficients show that the activity of the chloride ion varies widely among solutions of alkali chlorides at the same ionic strength [20]. Kester and Pytkowicz [21] showed that free ion activity coefficients are a function of the effective ionic strength of the medium, not the total ionic strength, since ion pairing changes the charge distribution and hence the free ion activity coefficients. Measurements of mean ion activity coefficients should therefore have been made in solutions of the same effective ionic strength as seawater. The assumption that the activity coefficients of charged species can be set equal to that of the bicarbonate anion was questioned by Pytkowicz [22] since "ion pairs are not covalently bound species and may show quite different behaviour to the bicarbonate anion." Similarly, one cannot assume that the activity coefficient of neutral species can be set equal to that of carbonic acid since, in slightly basic solutions such as seawater, the greatest fraction of carbonic acid determined analytically is hydrated carbon dioxide [22].

Although the model of Garrels and Thompson may be of limited use today because of the assumptions on which it is based, it broke new grounds in ocean chemistry. As stated by Skirrow [23] "The usage made of the concept of individual ionic

activities, the mean salt method and Debye-Hückel extrapolations are features of the method which will not appeal to the thermodynamic purists, but it must be remembered that the numerous ionic species present in seawater and the high ionic strength demand that some compromise be made if any progress is to be made in understanding the detailed ionic chemistry. The investigators must use whatever tools are to hand and Garrels *et al* (1961) have succeeded in setting up a model which should serve as a useful working model for future investigators."

Other models for the speciation of the major ions in seawater which are based on the Bjerrum ion association theory of ion pair formation, include the model of Kester and Pytkowics [21] and Pytkowics and Hawley [24]. An alternative approach is used in the model proposed by Whitfield [20], based on the Brønsted-Guggenheim hypothesis of specific ionic interaction [41]. The latter approach will not be dealt with in detail and it is sufficient to say that Whitfield concluded that his model is in agreement with those based on the ion association hypothesis.

Extension of the Garrels and Thompson model to include trace metals was carried out by Zirino and Yamamoto [25] and Dyrssen and Wedborg [26]. Since these models have similar features they will be discussed together. The model of Zirino and Yamamoto was constructed using individual ion activity coefficients (calculated from the Davies modification of the Debye-Hückel expression) and available and estimated thermodynamic stability constants for the reactions between the divalent metal ions, copper, zinc, cadmium and lead, and the anions chloride, sulphate, bicarbonate, carbonate and hydroxide. The model was used to calculate the degree of interaction between each of the metal ions and the anions as a function of pH. In addition to the abovementioned ionic constituents, Dyrssen and Wedborg included the heavy metal, mercury and the anions fluoride, phosphate and borate into their model. They avoided the use of single ion activity coefficients for the major ions by using stability constants determined in 0.7 moles dm^{-3} sodium chloride, however

constants for the species copper, zinc, lead and mercury were estimated from a compilation of non-critical formation constants [27]. Both models neglected the formation of chloride ion pairs with the major cations, however Dyrssen and Wedborg noted that sulphate ion pairing in seawater reduced the ionic strength from the formal value of 0.74 mol dm^{-3} to 0.66 mol dm^{-3}. (This was not taken into account in the selection of formation constants). In calculating speciation patterns both models assumed formation of aqueous mono, di, tri and tetra ligand complexes only, neglecting polynuclear and mixed ligand complexes. Solubility data and reactions with organic ligands were not considered.

The use of high speed computers has led to the development of more comprehensive models [28, 29, 30, 31, 32], two of the most recent being those of Motekaitis and Martell (1987) [28] and Turner, Whitfield and Dickson (1981) [29].

Motekaitis and Martell developed a model consisting of 167 complexes arising from 19 components to model the speciation of the metal ions in the surface water of the open ocean, considering only the inorganic complexes. The speciation patterns for a pH of 8.0, 8.1 and 8.2 were considered to be a base that may be used for the calculation of modifications in speciation that may occur as a result of changes in the temperature (not considered) and pressure (not considered)and from addition of various organic and inorganic ligands to take account of naturally occurring chelating agents or those that may be added through environmental pollution. The ligands EDTA (ethylenediaminetetraacetate), NTA (nitrilotriacetate), TTP (tripolyphosphate), citrate and SSA (sulfosalicylate - a model compound for humic acid) were added to the model singly, in the concentration range 10^{-9} to 10^{-7} mol dm^{-3}. Although the database was small, critical stability constants were used, and were adjusted to 0.7 moles dm^{-3} ionic strength using an empirical technique based on experimentally observed variations of stability constants with ionic strength for complexes of similar charge type [33]. Speciation determinations made included

equilibria with suspended solid phases such as hydroxides, carbonates and basic carbonates of the metal ions present. The formation of polynuclear complexes, mixed ligand complexes and chloride ion pairs was not considered.

The model of Whitfield and Turner was not intended to give a quantitative description of the chemical speciation of the ionic constituents of seawater nor to predict the effect of disturbances on the equilibria. Instead the aim of the authors was to correlate the speciation patterns of various elements and to place these studies in their logical context in relationship to the periodic table in order to highlight the underlying speciation patterns. For this reason the database was set up to cover as many elements in the periodic table as possible. It consisted of data for five hundred complexes formed from the interactions of fifty-eight elements with five ligands, without distinguishing the stoichiometry of the individual complexes. Polynuclear, mixed ligand complexes and chloride ion pairs were not considered, nor was the solubility of the species. Speciation of the major elements was calculated using the ion association model of Dickson and Whitfield [34] together with the computer program Haltafall [35], whereas that of the trace elements was calculated by hand from a set of linear equations similar to those used in the program. The model was extended to include the redox states of the metals as well as metal binding by humic substances. Constants for metal-humic binding were estimated or obtained from measurements made by Mantoura et al [32].

In the light of the work done so far, it was considered worthwhile to develop a model which would update, extend and improve existing models in order to gain further insight into the chemical speciation of biologically important elements in seawater. Although the database compiled by Motekaitis and Martell [28] comprises critical formation constants, it is relatively small. It was decided to extend this database to include other metals and ligands relevant to seawater and, where possible, to update the constants used. The concepts of metal speciation among

redox states, equilibria with solid phases and complexation with natural organic ligands, although covered singly to some extent by the models considered, need to be incorporated into one model. Similarly the formation of polynuclear and mixed ligand complexes, thought to be of significance for complex solutions such as seawater, yet which have not been considered by existing models needs to be included in the model.

In conclusion, perhaps it is advantageous to comment on the validity of the chemical modelling approach. All too often, the model is judged on its ability to represent reality [36]. This, however, should not be the fundamental aim of the modelling approach as, if it were to achieve this, it would by definition no longer be a model. Rather, the model should serve as an analytical technique to provide an understanding of the processes which control the chemical precipitation, dissolution, oxidation and reduction, as well as acid-base and coordinative interactions. [30].

1.3 OBJECTIVES

"The ultimate goal of research in support of chemical modelling, as in most scientific research, is the improvement of human life physically, emotionally and aesthetically through the understanding and prediction of processes and events. More immediate objectives include reliable speciation of trace elements, the objective (of which) is to predict toxicity and bioaccumulation in aquatic organisms and ultimately in man" [11].

Whereas the models discussed so far have come a long way in contributing to the understanding of ocean chemistry and hence to the goal of scientific research, we felt that a significant contribution could be made by the development of a model which would update, extend and improve existing models.

The objectives of this research are thus the following:

1. To construct an equilibrium model of the species relevant to seawater, together with reliable estimates of their concentrations.

2. To assemble a reliable thermodynamic database of protonation and complexation constants for all possible species based on a critical selection of these constants.

3. To use the equilibrium model and the database together with a suitable computer program to determine the speciation pattern of elements in seawater, taking into account the following:

   i. The inorganic speciation of the major ions Na^+, K^+, Ca^{2+}, Mg^{2+} and Sr^{2+} in seawater, and the effect of chloride ion pairing on the ionic strength including the formation of chloride ion pairs.

   ii. The inorganic speciation of all biologically important trace elements between their various oxidation states and amongst the inorganic ligands present including polynuclear and mixed ligand complexes.

   iii. The speciation of toxic heavy metals such as cadmium, lead and mercury and the effect of an increase in their concentrations.

4. Extension of the model to include the speciation of elements with naturally occurring organic ligands of which the fulvic acids are the most prevalent. To investigate the effect these ligands have on the inorganic speciation patterns of the trace metals.

5. Where possible to correlate results of the speciation model with experimental results reported in the literature.

6. Equilibrium constants for proton and metal carbonate complexes relevant to seawater conditions are poorly documented in the literature. If time permits we would like to measure some of these constants by potentiometry using glass electrodes.

CHAPTER TWO
THE MODEL

2.1 INTRODUCTION

A comprehensive, yet concise definition of chemical modelling, which is relevant to this study, can be found in the quotation from Jenne [11]: "Chemical modelling encompasses the aqueous speciation of dissolved cationic elements among organic and inorganic anionic ligands, of anionic elements among their complexes with cations and both cationic and anionic elements among their redox states. Chemical modelling also includes calculation of the degree of saturation of an aqueous medium with regard both to metastable and to equilibrium solids and calculation of sorption or desorption. Additionally, predictive chemical modelling must include kinetics".

The chemical model needs to be defined separately from the computer program which executes calculations based on the reference data and input data comprising the model [42]. Most models are constructed according to the Bjerrum ion association theory [40], yet within this framework there are two distinct but thermodynamically related techniques for solving the species distribution problem, that is, to find the most stable arrangement for a given solution. The first is the Gibb's free energy approach and the second is the so-called equilibrium constant approach. Both are subject to the conditions of mass balance and chemical equilibrium.

The Gibb's free energy approach first proposed by Dantzig and co-workers [43], involves minimizing the free energy function

$$\Delta G_m^{\theta} = -RT \ln K$$

for a given set of species subject to the restraints of the mass balance requirements.

The equilibrium constant approach proposed by Brinkley [44] is probably the most widely used by workers in this field of study. In this case the mass action expressions are substituted into the mass balance conditions resulting in a set of non-linear equations which are usually solved simultaneously through an iterative procedure, since an exact solution is not feasible. It has been suggested that for large complex systems the equilibrium constant approach is preferable, since at present there are more reliable and available equilibrium constants than free energy values [42].

The choice of the thermodynamic approach dictates the general category of mathematical techniques that need to be used. The Gibb's function approach makes use of Newton-Raphson, successive approximations and nested iterations. These techniques along with the thermodynamic formalism have been reviewed by Zeleznik and Gordon, who concluded that "any method of calculation that can be made reliable is a good method when equilibrium composition is the main concern" [45].

Various computer programs have been developed over the past few years to solve the mathematical calculations involved in the modelling of chemical equilibria. These differ from one another by the numerical techniques used and by the incorporation of additional features. The choice of a particular program is dependent upon the requirements which may vary from one study to another. The criteria for selection of a program for this study are the following: the program chosen should be able to handle equilibria between the solid, gas and aqueous phases; data for a large number of soluble species including mixed ligand and polynuclear complexes and several redox equilibria, as well as solubility data for several solids. Of the programs available in this laboratory, namely, COMICS [46], ECCLES [47], MINEQL [48] and REDEQL2 [49], the second generation REDEQL programs (MINEQL and REDEQL2) which are based on the use of the Newton-Raphson iterative convergence procedure are the obvious choice. MINEQL, is the

more compact of the two programs being more user friendly and flexible and was thus chosen for the work in this study. The additional features of the much more elaborate REDEQL2 were not required here.

The various procedures required in a modelling study can be represented by a flow diagram. Such a diagram is presented in figure 2.1 and indicates the proposed plan of approach to be used in this particular study.

The use of computer models to gain insight into the chemical processes of natural systems has been criticised on the grounds that since real systems are so complex, any model is bound to be a gross oversimplification. Yet much of chemistry relies on models of one type or another to give approximations of some real values, based on certain assumptions. For example, the Debye-Hückel equations and the MacInnes assumptions are both models which can be used to give approximate values for single ion activity coefficients in solution; the Langmuir adsorption isotherm is a theoretical model which predicts the adsorption of gas onto a surface, depending on the pressure of the gas in solution at equilibrium with the solid phase. If one wishes to use models of any kind to give insight into real processes, two important features need to be kept in mind: first, a model is not meant to represent reality, for if it were, it would no longer be a model, and second, the fact that the model is an oversimplification of the real system is a prerequisite for it being of any use at all. If a geographical map were to include all the details really present, it would be illegible and quite useless.

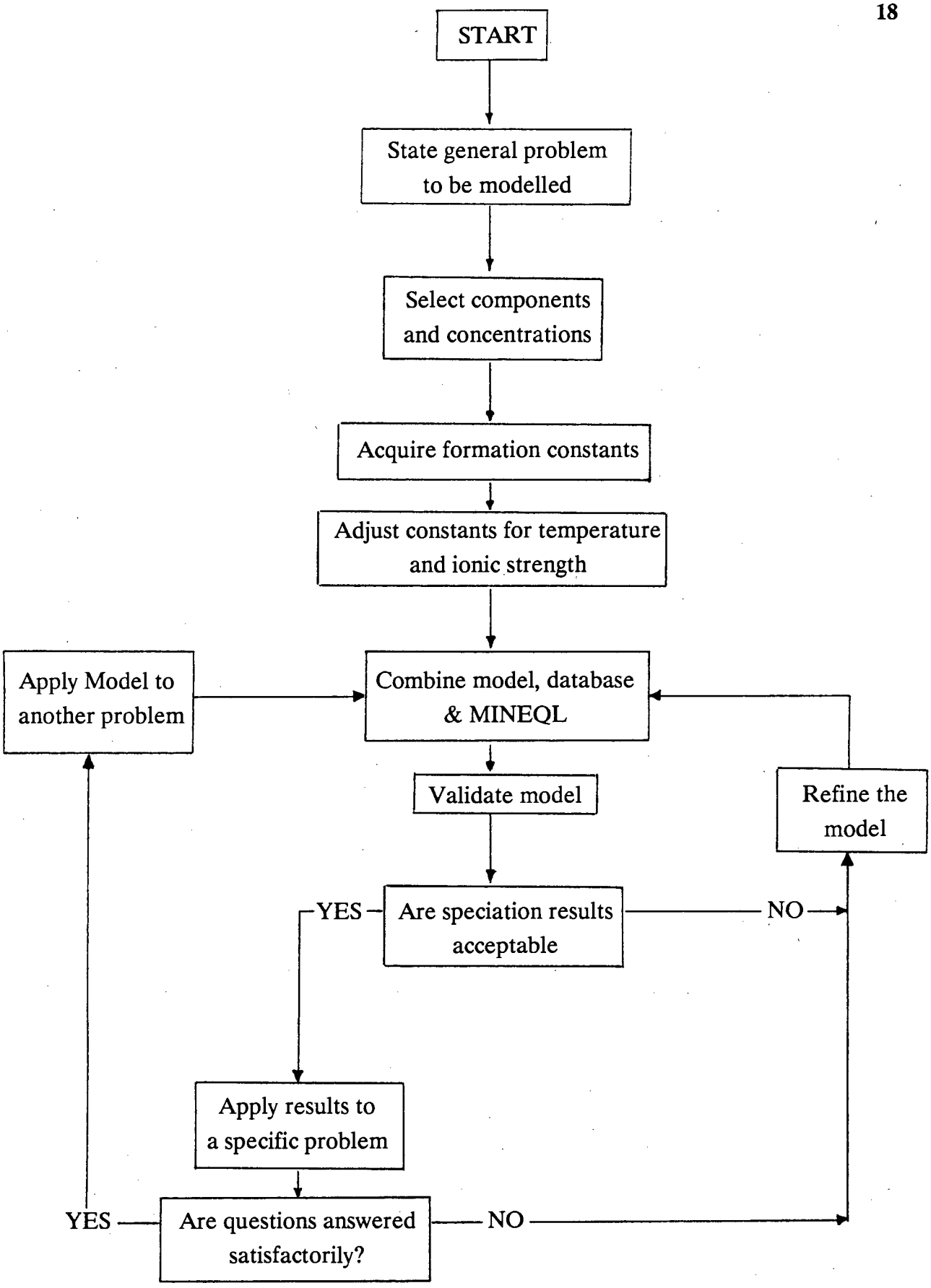


FIGURE 2.1: Flow diagram for chemical modelling procedure

2.2 THEORY

The thermodynamic basis of chemical modelling has been dealt with comprehensively in the literature [11, 43, 44]. The assumptions made are dependent upon whether the Gibb's free energy approach or the equilibrium constant approach is to be used. In this study the equilibrium constant approach is used.

The starting point of any modelling study involves choosing the components of the proposed chemical model, based on the composition of the medium to be modelled. Once the components have been selected it is necessary to determine all possible complexes that could arise from these components and to obtain formation constants for these complexes from the literature. Where a paucity of data exists, these constants need to be experimentally determined or estimated from values for similar systems. Often the latter approach is not very satisfactory if any quantitative determinations are to be made. In some cases an equilibrium constant is not directly available but values for the standard molar enthalpy and entropy of the species involved in the reaction are known. The following equation allows for calculation of log K from the standard molar enthalpy and entropy of the reaction:

$$\ln K = -(\Delta H_m^{\theta} - T\Delta S_m^{\theta})/RT \qquad 2.1$$

Having obtained the formation constants for the various complexes, many of these may require temperature and ionic strength adjustments to the temperature and ionic strength relevant to the study.

2.2.1 Correction of temperature

Temperature corrections are made using the van't Hoff equation applied to chemical reactions at constant pressure

$$(\partial(\ln K)/\partial T)_p = \Delta H_m^{\theta}/RT^2 \qquad 2.2$$

where ΔH_m^{θ} is the standard molar enthalpy of the reaction.

By assuming that ΔH is constant over a small temperature range the following approximation is obtained

$$\ln(K_2/K_1) = (\Delta H_m^{\theta}/R)(1/T_1 - 1/T_2)$$

2.2.2 Correction of ionic strength

Single ion activities and single ion activity coefficients cannot be measured experimentally. Estimates of the 'real' value can, however, be obtained using non-thermodynamic models, of which there are several based on the Debye-Hückel theory of estimating single ion activity coefficients. The Debye-Hückel theory describes single ion activity coefficient behaviour for ions in dilute solutions by considering long range electrostatic interactions between ions of opposite charge. It can be extended to solutions of higher ionic strengths through the use of adjustable parameters which take into account the short range non-electrostatic interactions important in more concentrated solutions. The general form of the extended Debye-Hückel equation is

$$\log \gamma_i = A z_i^2 I^{0.5} / (1 + B\mathring{a}_i I^{0.5}) + C I \qquad 2.3$$

where γ_i is the activity coefficient of ion i, A, B are constants dependent upon the dielectric constant, temperature and density of the solution.

The basic difference between the models is the choice of values for the B, å and c parameters as can be seen from table 2.1.

Recently, a computer program, LOGK [50], has been developed in our research group, based on a form of the extended Debye-Hückel equation (equation 2.3) which is able to correct formation constants for ionic strength from as few as one or two literature values at different ionic strengths. This program was developed as part of a project on setting up a computer model for soil equilibria and results of an extensive survey showed it to be of sufficient accuracy for correction of formation constants to an ionic strength of 0.04 mol dm^{-3} from values as high as 2 mol dm^{-3} or 3 mol dm^{-3} [51]. A second advantage is its ability to correct formation constants reliably from as few as one or two other values.

The setting up of a database for a seawater model involves the aquisition and correction for ionic strength of a large number of formation and protonation constants. For this reason the computer program, LOGK, was chosen as an efficient and sufficiently accurate means of accomplishing this task.

A brief description of the theory behind LOGK will now be given. For a given complexation reaction between a metal ion , M and a ligand, L

$$pM + qL = (M_pL_q) \qquad 2.4$$

the equilibrium constants K_1 and K_2 at ionic strengths I_1 and I_2 are related by

Table 2.1 Equations for the calculation of individual ion activity coefficients

Model	Equation	Approximate range of validity	References
D-H Limiting Law	$\log \gamma = -Az^2I^{1/2}$	$<10^{-2.3}$	[14]
		$<10^{-3}$	[133]
Extended Debye-	$\log \gamma = -Az^2I^{1/2}/(1 + B\text{å}I^{1/2})$	$<10^{-1}$	[14]
Hückel		$<10^{-2}$	[133]
Hückel/Linder	$\log \gamma = -Az^2I^{1/2}/(1 + B\text{å}I^{1/2}) + B'I$		
& Murray		> a few molar	[133]
Güntelberg	$\log \gamma = -Az^2I^{1/2}/(1 + I^{1/2})$	<0.1	[14]
Guggenheim	$\log \gamma = -Az^2I^{1/2}/(1 + I^{1/2}) + B'I$	<0.5	[133]
Davies	$\log \gamma = -Az^2\{I^{1/2}/(1 + I^{1/2}) - 0.2I\}$	<0.2	[133]
		<0.5	[14]
Scatchard	$\log \gamma = -Az^2I^{1/2}/(1 + 1.5I^{1/2})$	<0.2	[133]
Datta & Grzybowski	$\log \gamma = -Az^2I^{1/2}/(1 + I^{1/2}) + B'I + C'I^{1.5}$	<0.2	[133]

B', C' are adjustable parameters, values of which are different in the different equations.

$$K_2 = Q_2K_1/Q_1 \qquad 2.5$$

where Q is a quotient of activity coefficients for the reaction at a given ionic strength.

The activity coefficient of the product and reactants may be calculated from equation 2.3, provided that values of å and c are available. Kielland [52] and Truesdel and Jones [53] have listed values of å for a wide range of ions. When values are not available the following formulae can be used:

$$\text{for small organic ions } å_i = z_i + 4$$
$$\text{for inorganic ions } å_i = 2z_i + 2$$

This makes the assumption that ionic strength does not affect the activity of uncharged species. By assuming that the c parameter has the same value for each ion in equation 2.4, an overall value of c for the system may be calculated and used for predicting the formation constant at a different ionic strength.

If a literature value for the formation constant is available at only one ionic strength, the value of c cannot be determined by the above procedure and instead is set equal to -0.10, the value recommended by Davies for 1 : 1 electrolytes [51].

The adjustment of solubility products was carried out using an analogous procedure to the one given above. The computer program LOGKSP [54] was used for continuity since it is based on the same assumptions as LOGK.

The results of an error analysis conducted by Linder and Murray [51] show that in most of the cases considered, the reported constants are a greater source of error

than the ionic strength adjustments made, particularly if these adjustments are made for small ionic strength differences.

2.2.3 Redox equilibria

It is convenient to define the relative electron activity in aqueous solution by analogy with the former definition of pH, namely

$$pH = -\log\{H^+\}$$

The expression for electron activity is

$$pE = -\log\{e^-\}$$

where $\{H^+\}$ represents the absolute activity of 'free' i.e. hydrated protons in moles dm^{-3} and $\{e^-\}$ represents the activity of the electron relative to the standard hydrogen electrode of unit activity.

Equilibrium relationships involving oxidation and reduction reactions can either be expressed in terms of an equilibrium constant, K^θ or the standard electrode potential for the reaction, E^θ. The half cell reaction is written as

$$\text{oxidised} + ne^- = \text{reduced}$$

For which E^θ is related to K^θ by the well known expression

$$E^\theta = 2.303\ R\ T\ \log K^\theta / nF \qquad 2.6$$

Often the redox potential of natural systems is given in terms of the parameter E_h, the potential of the system relative to the hydrogen half cell. E_h can be converted to pE using the following equation

$$pE = (F / 2.303\ R\ T)E_h$$

2.2.4 The formation of ternary mixed ligand complexes

It is now generally agreed that in a solution containing metal ions and two different *suitable* ligands, mixed ligand complexes will be formed [55, 56, 57]. This is particularly relevant for multi-metal-multi-ligand systems such as seawater [58] and biological fluids, where a mixed ligand complex forms an intermediate in the catalytic actions of metal chelates and enzymes [56].

The enhanced stability which mixed ligands show over their binary counterparts has been attributed in part to statistical effects. Watters [56] demonstrated that the formation of the mixed ligand complex, MAB, from a metal ion, M in the presence of equal concentrations of ligands A and B, is always three times more favourable statistically than the formation of MA_2 or MB_2. Often mixed ligand complexes are more stable than would be expected from solely statistical considerations. This enhanced stability has been attributed to ligand-ligand interactions, geometric factors, dipole interactions with the solvent and outer versus inner orbital coordination [50]. It is important to bear in mind that in some cases these factors can also result in destabilization of the mixed ligand complex relative to the binary complexes.

For the general reaction between a metal, M and two ligands of equal denticity, A and B:

$$i/n\ MA_n + j/n\ MB_n = MA_iB_j \qquad 2.7$$

where i, j are the stoichiometric coefficients of A,B in the ternary complex and n = i + j.

The equation for the calculation of the formation constant for the mixed ligand complex is given by

$$\log\beta_{ij} = \log K_m + i/n \log\beta_{n0} + j/n \log\beta_{0n} \qquad 2.8$$

where β_{no} and β_{0n} are the formation constants for the complexes MA_2 and MB_2 respectively and K_m is the "mixing constant" for equation 2.7.

K_m includes both statistical and non-statistical contributions to the stability of the ternary complex.

$$\log K_m = \log K_s + \log (n/i)$$

where $\log K_s$ is the stabilization constant and is a measure of the non-statistical contributions and $\log (n/i)$ represents the statistical contribution.

In order to make meaningful comparisons between the stability of the mixed complex, relative to the binary complexes, using the mixing constant K_m, several factors must be considered:

a)Ideally, the ligands should be of the same denticity and charge, so that the binary complexes and the ternary complex are all of the same charge and have the same coordination level.

b)The geometric configuration of the binary and ternary complexes should be the same.

c)Measurements of binary constants should be carried out under the same conditions as those for ternary complexes.

Generally it is found that values for log K_s are small, lying between the limits -0.5 to +1.0 [55], hence statistical effects provide a good first approximation. If for some reason meaningful values of K_m cannot be calculated, the formation constant for the mixed species, β_{ij} can be approximated by replacing log K_m with the statistical term log (n/i).

2.2.5 The thermodynamic basis of the chemical speciation problem.

The problem of solving the chemical speciation pattern by either the Gibb's free energy approach or the equilibrium constant approach, involves finding the unique solution to a set of non-linear, simultaneous equations using an iteration procedure. Since MINEQL uses the equilibrium constant approach the rest of the discussion will be specific to this approach and peculiar to the program MINEQL.

In order to illustrate the principles involved we can consider a system in which there are **n** components which react to give **m** complexes. Given either the total or free concentrations of every component, the objective is to calculate the concentrations of all the constituents which exist in equilibrium in the well defined single phase mixture. Generally, the system is defined in terms of the total concentration of each component and only a few free concentrations are known. For example, the concentrations of free hydrogen ions can be determined from glass electrode measurements and the concentrations of some metals and ligands may be determined from ion-selective electrode measurements. Initially, only the solution phase is considered. The concentration, C_i of each complex species i, can be expressed as a function of the free concentration of each of its components, together with its cumulative formation constant β_i, and is fixed by the Law of Mass Action:

$$C_i = \beta_i \prod_{j=1}^{n} X_j^{a(i,j)} \quad \text{,for } i = 1, m \qquad 2.9$$

where C_i is the concentration of complex i, β_i is the stability constant for the formation of i, X_j is the concentration of component j, and a(i,j) is the stoichiometric coefficient of component j in complex i.

It is important to note that where n = 1, the complex C_i is equivalent to the free component X_j. To calculate the speciation of the system, m equations of form 2.9 are required. Since for the majority of the components only the total concentrations are known, the concentration of each complex is calculated from an initial guess of the free concentration of each component, X_j. The problem is thus essentially reduced to finding the set of free concentrations of all components in the solution that will satisfy the mass balance condition for each component. This condition states that the total calculated concentration of component j is given by the sum of the free concentration of that component, together with the amount of j in all the complexes. The calculated total concentration can then be compared to the imposed analytical total concentration, T_j by means of the difference function

$$Y_j = \sum_{i=1}^{m} a(i,j)(C_i) - T_j \qquad 2.10$$

where T_j is the total analytical concentration of component j and Y_j is the difference between the total analytical concentration and the calculated total component concentration.

The exact solution to the problem is thus the set

$$\{X_j : j = 1, n\}$$

such that all Y_j's = 0. To solve the problem MINEQL calculates the concentration of each complex, C_i, using initial estimates of the free component concentration X_j. The total concentration of each component is then calculated and by the use of the Newton-Raphson method, the difference function Y_j for each component, together

with its derivatives are used to find improved values for the X_j's. These are then resubstituted into equation 2.9 and the process repeated until the Y_j's are minimised.

Since in practice the root of the equation $Y(X) = 0$ is not correct, some criterion must be established such that when, by iteration, each Y_j becomes sufficiently close to zero, the system of equations is said to be "solved". Since each Y_j is a sum of terms which vary widely in order of magnitude, the convergence criterion is chosen to reflect the magnitude of Y_j relative to the maximum of the terms of which Y_j is the sum. Thus the criterion for convergence is given by

$$\frac{|Y_j|}{\max(Y_j)} < \epsilon \quad \text{for } j = 1,n$$

where $\max(Y_j)$ is the maximum of the absolute values of the set of terms in equation 2.10 of which Y_j is the sum and ϵ is a small positive number, specified by the user.

In order to avoid matrix inversion the iterative formula from the Newton-Raphson method of solving the roots to the equation $Y(X) = 0$, is modified and the resulting Jacobian is solved by Gaussian elimination. Furthermore, to improve the efficiency of computation, MINEQL makes use of a transformation of basis, with the result that the Jacobian approaches a diagonal matrix, leading to faster solution of the problem.

Once convergence has been obtained MINEQL then calculates the degree of supersaturation with respect to the potential solid phases. If it occurs that the product of the free concentrations exceeds the solubility product for any complex, precipitation of that complex is then indicated. This effectively changes the free

concentration of these components, and the problem has to be modified. Solution to the problem is again found by iteration, using the new estimated free concentrations as starting values. It can happen that a solid which has precipitated may redissolve, resulting in an effective increase in the free concentrations of the components. Only once no further dissolution or precipitation occurs is the problem taken as being solved.

2.3 CONSTRUCTION OF THE MODEL

2.3.1 Selection of components

Eleven components together account for more than 99.5 percent of the total dissolved solids in seawater. These constituents together form the major conservative species, present in millimolar concentrations and are well mixed throughout the ocean. As a consequence, their concentrations exhibit an almost constant ratio to one another, although the total concentration of dissolved inorganic constituents usually ranges between 33 and 37 grams per kilogram of seawater. This constancy of composition has been reported in the literature as early as 1819, (see review by Culkin [59]).

In addition to the major ionic constituents, seawater also comprises most of the elements in the periodic table [29]. Although only present in nanomolar concentrations these trace elements are involved in important inorganic and biochemical reactions in the marine environment, and must necessarily be included in the model. It is almost impossible to obtain an average concentration for the minor elements since their concentrations are not as uniform as those of the major ions. Even in the open ocean, the concentration of the trace elements may vary five-fold, depending upon factors such as the degree of adsorption on to particulate matter and uptake by microorganisms. In addition, experimental measurement of total concentration at the nanomolar level is extremely difficult, contributing to the variation in the reported concentrations.

The set of components used in this seawater model, together with their concentrations relevant to surface seawater at 25°C and 0.1M ionic strength is given in table 2.2. Coverage of the major and minor elements is as wide as possible, based on components for which 'reliable' concentrations are available. The concentrations

of the major constituents, except for strontium, as well as those of some of the minor constituents were taken from results of a survey conducted by Ahrland [60] and represent the mean of values given in several other compilations [17, 59, 20, 29]. Components and concentrations not referenced in Ahrland, were taken from an average of the values given in the above references.

As can be seen from table 2.2, the electron is taken into account as one of the components, since it is required for the redox equilibria. As pointed out by Sillén [62], the electron can be treated like any other reactant or product in a chemical reaction. The theoretical concept of 'free electrons' in solution is particularly useful in equilibrium studies since all the equilibria can be written in terms of concentrations. Since one of the objectives of this study is to consider the speciation pattern arising from distribution of the metals amongst their different oxidation states, those states have been listed as components although the particular micronutrient is only input in one particular form.

Protons are considered as arising from the dissociable hydrogen ions of protonated ligands and therefore have an input concentration. Hydroxyl ions are taken into account implicitly by including the ionic product of water amongst the equilibria in the database and need therefore not be listed as a separate ligand. The model is considered to be in gaseous equilibrium with the atmosphere. Oxygen and carbon dioxide are implicitly considered by the use of conditional equilibria and are thus not input as components as such. This will be elaborated upon in sections 2.3.2.5 and 2.3.2.4 respectively.

Table 2.2: Components and concentrations used in the seawater model

Major components /10^3 mol dm^{-3}

cations	total conc	anions	total conc
sodium	479	chloride	559
magnesium	545	sulphate	28.9
calcium	10.5	carbonate	2.35
potassium	10.4	silicate	0.22
strontium	0.09	borate	0.4
lithium	0.025	bromide	0.86
protons	3.67	fluoride	0.08
		electrons	0.00

Minor components /10^9 mol dm^{-3}

component	total conc	component	total conc
iron	8	cobalt	0.9
copper	4	silver	0.4
zinc	5	cadmium	0.1
nickel	5	cromium	6.3
manganese	4	uranium	14
mercury	0.02	tin	0.1
lead	0.05	phosphate	200
aluminium	79	nitrate	100
		iodine	501

2.3.2 Compilation of the database and the acquisition of formation constants and solubility products

It is generally accepted that the largest source of error associated with setting up of a model is contributed by errors in the reported equilibrium constants. In order to minimise this source of error, equilibrium constants for the roughly 470 equilibria arising from interaction of the components given in table 2.2 were taken from the critical compilations of stability constants of Smith and Martell [37, 38, 39]. Constants for the hydrolysis of metal ions were taken from Baes and Mesmer [63]. Rigorous selection criteria were employed by Smith and Martell on compilation of these critical tables and determination of the reliability of a particular constant was based on the following:

the method of determination,
the author of the paper,
the journal of publication,
specification and control of temperature and ionic strength,
information on the purity of the ligand, nature of the supporting electrolyte and calibration of apparatus,
the constant being representative of the values reported by other workers.

Initial modelling results showed certain species to have a marked effect on the speciation pattern. In particular, the precipitation of certain solids caused marked variations in the modelling results. In such cases the accuracy of the constant used in the model is of great importance and a more detailed discussion on the range of reported values will be given. Solids which appear to affect the speciation pattern through precipitation or which are near to saturation as determined by their solubility products include the following: magnesium carbonates, calcium carbonates and iron hydroxide. Some dissolved species such as the mixed ligand complexes and the iron-borate complexes appeared to be present in relatively high amounts, and as such also affect the speciation pattern. These constants together

with the constants for the two gaseous equilibria will therefore be discussed in more detail.

2.3.2.1 The solubility product of iron(III) hydroxide

The choice of solubility product of iron(III) with hydroxide is rather difficult since a wide range of values for the constant can be found in the literature. The scatter of reported values can be attributed in part to the type of precipitates formed by iron as well as to the transformations which those precipitates undergo on ageing.

The thermodynamically stable form of precipitated iron(III) hydroxide, FeO(OH), is often only formed after several years of ageing [63]. Schindler (1963) [63] reports a value for the logarithm of the equilibrium constant for the following reaction of -1.4 in 3 mol dm^{-3} $NaClO_4$:

$$Fe^{3+} + 3H_2O = FeO(OH) + 3H^+ + H_2O \qquad 2.11$$

A thermodynamic value of log K of -0.02 was determined by Lindsay for the reaction 2.11 from the thermodynamic data of Schmatz (1959) [63].

The formation of amorphous iron(III) hydroxide, reaction 2.12, is characterised by a range of log K values from -4.9 at 0.0 mol dm^{-3} as determined by Langmuir on freshly precipitated solid [64] to -2.5 at 0.0 mol dm^{-3} reported by Schindler on aged amorphous precipitate [63].

$$Fe^{3+} + 3H_2O = Fe(OH)_3\,(s) + 3H^+ \qquad 2.12$$

Byrne and Kester [64] determined a value for hydrous iron(III) oxide precipitated from seawater of log K = -5.67. This corresponds to a value of -4.5 at 0.0 mol dm^{-3} which is in close agreement with the value of Langmuir. Biedermann and Schindler

studied the steady state reached after 200 hours with amorphous iron(III) hydroxide in 3 mol dm^{-3} $NaClO_4$ at 25°C [63]. Their value for log K of -3.96, adjusts to a value of -2.98 at 0.0 mol dm^{-3}.

As the model is based on thermodynamic equilibrium a decision had to be made as to whether the solubility of iron(III) in the model should be based on the solubility product of either the amorphous iron hydroxide or the α-FeO(OH) form, and secondly as to which value of the solubility product should be used. The models reviewed in the introduction, with the exception of that of Motekaitis and Martell [28], do not consider the solubility of the dissolved transition metal complexes. Martell used a log K value of -2.77 for reaction 2.12. This value is obtained from reference [39] corrected to 0.1 mol dm^{-3} by the use of adjustment factors.

A model of Kester *et al* [65] on the speciation of iron in marine systems, considers the species $Fe(OH)_3$ as a solution complex. The more recent publication of Byrne and Kester [64] however gives a value for the solubility product of iron(III) hydroxide precipitated from seawater (loc. cit.). Uncertainty as to the nature of the molecular structure of the neutral $Fe(OH)_3$ species arises from interpretation of results from filtration experiments, either in terms of uncharged complexes or in terms of very small colloidal particles. Nordstrom *et al*, in their investigations using WATEQ2 [40] use a value for log K of -4.90 for the precipitation of amorphous iron(III) hydroxide, which they obtained from data of Langmuir and Wittemore [66].

On consideration of the above, it was decided to include the solid amorphous $Fe(OH)_3$ in the model for seawater. The value of 38.8 as given in reference [38], was chosen as a representative value for the logarithm of the solubility product. From this value, a log K for reaction 2.12 of -3.80 at 0.7 mol dm^{-3} was determined using LOGKSP [54].

2.3.2.2 Stability constants for the iron borate complexes

Preliminary modelling results showed the iron(III) borate species to be predominant for iron(III), which is contrary to several other reports [65, 67] in which these species were shown to be insignificant.

The values of log K for the formation of $FeB(OH)_4^{2+}$ and $Fe(B(OH)_4)_2^{+}$ as given in reference [39] are 10.85 and 22.4 (0.7 mol dm^{-3} and 25°C) corresponding to reaction 2.13 for n = 1,2 respectively.

$$Fe^{3+} + n\,B(OH)_4^- = Fe(B(OH)_4)_n^{(3-n)+} \qquad 2.13$$

It appears that these constants are in error when compared to the original reference [67] from which these values have been taken. Elrod and Kester quote values of log K of -2.0 and -4.68 respectively for the following reactions:

$$Fe^{3+} + B(OH)_3 + H_2O = FeB(OH)_4^{2+} + H^+$$

$$Fe^{3+} + 2B(OH)_3 + 2H_2O = Fe(B(OH)_4)_2^{+} + 2H^+$$

which can be put into the form of equation 2.13 by combination with the protonation reaction for boric acid:

$$B(OH)_4^- + H^+ = B(OH)_3 + H_2O$$

The logarithm of the protonation constant for boric acid is taken as 8.85 by Elrod and Kester, but the value of 8.41 given in reference [39] has been used in the model. The resultant values of log K for the formation of $FeB(OH)_4^{2+}$ and $Fe(B(OH)_4)_2^{+}$ are 6.41 instead of 10.85 and 12.14 instead of 22.4.

2.3.2.3 The solubility products of calcium and magnesium carbonates

Results of initial modelling studies showed the solid calcium and magnesium carbonates to be of importance as they frequently precipitated from solution. Besides their importance in regulating the solution composition through precipitation and removal of ions from solution, these species may be expected to play an important role in regulating the pH of the solution through their involvement with the carbonate equilibria.

Determination of the solubility products of calcite and aragonite at low ionic strengths have been carried out by several investigators (Backstrom 1921; Frear and Johnson 1929; Miller 1957; Yanat'yeva 1954; Grezes and Basset 1965 (see Langmuir [68]) and Nakayama [69]). Since there is good agreement between the reported values, despite the different techniques used the values given in reference [39] of -8.35 and -8.22 for the negative logarithm of the solubility products of calcite and aragonite respectively are a good representation of the thermodynamic solubility products.

The apparent solubilities of synthetic calcite and aragonite in natural or synthetic seawater have been determined by several different investigators (Ingle 1973; MacIntyre 1965; Jacobson and Langmuir 1974; Plath 1978 (see Morse *et al* [70]); Morse, Mucci and Millero 1980 [70]; Berner 1975 [71] and Berner 1976 [72]) and in general have been found to be 20% and 22% less for calcite and aragonite respectively, than values calculated from thermodynamic constants and activity coefficients [70]. This substantial difference between measured and calculated values has been attributed to the formation of surface layers of lower solubility than the pure solid (calcite) and slow precipitate inversion on ageing (aragonite) [70]. Morse *et al* measured a value for the apparent solubility of synthetic calcite of 4.36 x 10^{-7} mol^2 kg^{-2}, which is in good agreement with the values proposed by Ingle (1973),

MacIntyre (1965) and Plath (1979) [70]. Determination of the apparent solubility of synthetic aragonite in seawater made by different investigators are however in poor agreement. A consistent trend in the results is a decrease in the measured apparent solubility with increasing time of equilibration. The value determined by Morse *et al* for an equilibration time in excess of two months (ie 6.65 x 10^{-7} mol^2kg^{-2}) is significantly larger than that determined by Plath (1979) (9.46 x 10^{-9} mol^2kg^{-2}) and Berner (1976) (8.21 x 10^{-9} mol^2kg^{-2}), both of which are based on equilibration times of only a few days.

Instead of using thermodynamic solubility products adjusted to 0.7 mol dm^{-3}, apparent solubility products for calcite and aragonite have been used, since by taking into account slow inversion and the formation of a surface phase of lower solubility these values reflect more closely the real system. The values of Morse *et al* for the apparent solubilities of synthetic calcite and aragonite in natural seawater have been used in the model. As stated before the value for calcite solubility is in good agreement with that of other workers, while that of aragonite, although lower than that of other workers was carefully determined, the authors having taken account of the effects of different solid to solution ratios and equilibration times. For the purpose of modelling ,the constants were converted to the molarity scale (the density of 35% seawater at 25°C was taken as 1.0265 gcm^{-3} [79]) and expressed as the logarithm of the formation constant for the solid phase. Hence the logarithms of the values used for calcite and aragonite are 6.35 and 6.15 respectively.

Solubility products reported in the literature for the magnesium carbonates are not well defined. Magnesium carbonate precipitates from solution in several different forms, the solubilities of which increase in the following order : $MgCa(CO_3)_2$, dolomite; $MgCO_3$, magnesite; $MgCO_3.3H_2O$, nesquehonite and $MgCO_3.5H_2O$, lansfordite. Solubility constants reported in the literature for magnesite vary by a

factor of five. Values for the logarithm of the solubility product vary between -8.20, determined by Robie and Hemingway to -7.46 determined by Halla [14] (both 0.0 mol dm^{-3}). The latter value has been adjusted for ionic strength and used in the model as it is also the value recommended by Smith and Martell [38]. The logarithm of the solubility product for dolomite shows an even larger range from -16.5 to -19.3 at 0.0 mol.dm^{-3} [14]. The value of -17.0 determined by Langmuir [68] was used in the model as a representative value. Adjustment to the ionic strength of 0.7 mol dm^{-3} gave a value of -14.58.

2.3.2.4 The carbonate equilibria

In setting up the model it is assumed that the aqueous phase is in equilibrium with carbon dioxide. Unlike other atmospheric gases, carbon dioxide reacts readily with water according to the following reaction:

$$2H^+ + CO_3^{2-} = H_2CO_3^* = CO_2(g) + H_2O \qquad 2.14$$

where $H_2CO_3^*$ represents the uncharged ion pair H_2CO_3 and aqueous CO_2 in a ratio of about 1 : 650 [14].

A value for the logarithm of the equilibrium constant for equation 2.14 can be obtained by splitting it up into the following reactions:

$$H^+ + CO_3^{2-} = HCO_3^-$$

which has a log K of 10.33 [38] at 0.0 mol dm^{-3} and

$$H^+ + HCO_3^- = H_2CO_3^*$$

with a corresponding log K of 6.351 [38] at 0.0 mol dm^{-3}. This gives an overall protonation constant of log K = 16.68 at 0.0 mol dm^{-3} for the reaction:

$$2H^+ + CO_3^{2-} = H_2CO_3^* \qquad 2.15$$

The solubility of gaseous carbon dioxide in water, described by the reaction:

$$CO_2(g) + H_2O = H_2CO_3^*$$

has a value of log K = -1.466 [73] at 0.0 mol dm^{-3}, which takes the vapour pressure of water into account. Combining this with reaction 2.15 a value of log $K_{(g)}$ of 18.146 (0.0 mol dm^{-3}) can be obtained for reaction 2.14.

If the partial pressure of carbon dioxide is taken as fixed at $10^{-3.5}$ atmospheres for atmospheric conditions it follows that the quotient

$$H_2O/[H^+]^2[CO_3^{2-}]$$

has a value of log K′ = 21.65 at 0.0 mol dm^{-3} and 25°C. This is the form of the reaction as required for input into MINEQL. Adjustment of this constant to 0.7 mol dm^{-3} ionic strength using the program LOGK [51] results in a value of 20.80, which was used in the model.

2.3.2.5 Redox speciation and the equilibria of dissolved oxygen

In constructing an equilibrium model as a counterpart to the real ocean, certain simplifying assumptions need to be made. The first of these concerns the redox state of the ocean. Much of the chemistry of seawater can be sufficiently well approximated by an equilibrium model since the rates of most physical and chemical processes are slow on the time scale of consideration giving rise to a time invariant

steady state. Although the redox processes operating in the ocean are slow and the components can be characterised by a nearly steady state composition, there is a lack of coupling between these processes, a consequence of which is that the redox state of the real system cannot be characterised by a unique pE [74, 14, 75].

In order to simplify the system several attempts have been made at determining a dominant couple which would regulate the redox level of other less abundant redox couples. The proposal of Sillén [76] that the oxygen-water couple is the predominant redox buffer which determines the redox state of surface seawater is generally accepted as being the most likely. Oxygen is more abundant in the atmosphere, within the time span of its residence time, than in the other accessible exchange reservoirs. It is biologically and chemically reactive; its redox processes (photosynthesis and respiration) occurring ten times more rapidly across the sea-air interface than that of the other atmospheric gases. Moreover, if the full four electron reduction of oxygen to water occurs, as in the case of biologically mediated redox reactions, oxygen is a strong oxidant.

Modelling in the presence of the oxygen-water couple requires incorporation of the oxygen redox half-cell reaction

$$¼O_2(aq) + H^+ + e^- = ½H_2O \qquad 2.16$$

which has a log K value of 20.78 (0.0 mol dm^{-3}). Assumption of a constant partial pressure of oxygen of 0.2095 atmospheres, gives a conditional value of 20.61 for the quotient

$$[H_2O]^{0.5}/[H^+][e]$$

This adjusts to a value of log K 20.30 relevant to 0.7 mol dm^{-3} , which was included in the model for the oxygen redox reaction.

The proposal of Sillén that biological mediation of the four electron reduction of oxygen to water results in this being the dominant redox couple has been challenged by Breck [77]. Instead he proposed that the two electron reduction of oxygen to peroxide is the predominant couple owing to the kinetic difficulty associated with breaking the oxygen to oxygen bond.

$$O_2 + 2e^- + 2H^+ = H_2O_2 \qquad \log K = 23.1$$

In order to include this reaction in the model, as an alternative to the oxygen-water couple, it is necessary to know the peroxide activity in seawater, for which reliable estimates are not available. The ready decomposition of peroxide to oxygen and water, which is catalysed by a host of metals and non-metals in seawater results in a peroxide activity which is small and variable and therefore analytically difficult to measure. Breck assumes a value of 10^{-11} for the peroxide activity in seawater. Based on this value and the constant partial pressure of oxygen, a conditional constant of log K 16.70 (0.0 mol dm^{-3}) can be calculated. This gives a value of 16.37 at 0.7 mol dm^{-3}.

2.3.2.6 The formation constants for the mixed ligand complexes

Mixed ligand complexes are likely to form in multi-electrolyte solutions such as seawater, where the ligands are present in relatively high concentrations. Dyrssen and Wedborg [26] have indicated that these complexes may be important for copper, zinc and mercury in seawater. In order to ascertain the possible importance of such species, constants for the formation of mixed halide complexes as well as hydroxy-phosphate species were estimated according to the equation 2.8 and incorporated into the model. The mixed halides were chosen because of the high concentrations of the halides in seawater, whereas the hydroxy-phosphate species were chosen because both ligands form strong binary multi-ligand species with

metals. For some hydroxy-phosphate complexes, values for an ML_2 species, where M represents the metal and L the ligand, were not available from the literature. A value two to three log units larger than the formation constant for the ML species was then used in equation 2.8 as an estimate of the formation constant for the ML_2 species. In some cases, experimentally determined values for the formation of ternary halide species were available [55, 78] and in general, the values estimated from equation 2.8 compared favourably with the experimentally determined values. In order to illustrate the method used for the estimation of constants, the steps involved in the estimation of the formation constant for the complex formed between zinc, hydrogen phosphate and hydroxide will be discussed in more detail. The log K values for the formation of the binary species $Zn(OH)_2$ and $Zn(HPO_4)_2^{2-}$ are 9.0 and 1.86 respectively. These values, together with a statistical term of log 2, are used in equation 2.8 to estimate a value for the formation of the mixed ligand complex $Zn(OH)(HPO_4)^-$ of log K = 5.73 at 0.7 mol dm^{-3} according to the following reaction

$$Zn^{2+} + OH^- + HPO_4^{2-} = Zn(OH)(HPO_4)^- \qquad 2.17$$

This however is not the overall formation constant as the protonation of the phosphate anion needs to be taken into account:

$$H^+ + PO_4^{3-} = HPO_4^{2-}$$

Combination of this protonation constant, log K = 11.4 (0.7 mol dm^{-3}), with the equilibrium constant for reaction 2.17 gives a log K value of 17.13 for the overall reaction

$$Zn^{2+} + OH^- + H^+ + PO_4^{3-} = Zn(OH)(H)(PO_4)^- \qquad 2.18$$

Since the hydroxide ion is not a component in MINEQL, it is necessary to express the formation of the ternary species in terms of the reactants zinc, phosphate and water

$$Zn^{2+} + PO_4^{3-} + H_2O = Zn(OH)(H)(PO_4)^-$$

In order to do this, reaction 2.18 is combined with the reaction for the dissociation of water

$$H_2O = H^+ + OH^-$$

which has a log K value of -13.77 at 0.7 mol dm^{-3}. This results in a formation constant of 3.66 for the formation of the mixed ligand complex $Zn(OH)(H)(PO_4)^-$.

Even though this ternary species may have the same stoichiometry as a binary complex, the program recognises them as separate species each with its own concentration. In order to prevent confusion on the part of the user, the ternary complexes in the database have been designated an identification number starting with '9' as opposed to the '7' indicative of dissolved complexes.

2.3.3 Temperature and ionic strength adjustments

Formation constants in the seawater database are valid for a temperature of 25°C. Although this value is close to the upper limit for surface seawater, it is the temperature at which most of the constants given in the critical compilations [37, 38, 39] have been determined. Thus by setting up a database at 25°C, the scope of reactions for which constants are available without having to make adjustments from thermodynamic data was kept as broad as possible. A second advantage is that in the few instances where temperature adjustments were necessary, these were

made over small temperature ranges, thus justifying the assumption of a constant ΔH_m^{θ}.

Adjustment of the constants from the ionic strength at which they were measured to that of seawater was carried out using the program LOGK and LOGKSP, for dissolved and solid species respectively. Where both a conditional value and the thermodynamic value were available for a particular constant, the conditional value was chosen in preference, since the assumptions made in extrapolating to zero ionic strength for the thermodynamic constant were not known.

Initially when faced with the task of setting up a database, a decision had to be made as to whether the constants included should be valid for zero ionic strength and corrected to the ionic strength relevant to the modelling study by the program MINEQL or whether the database should be set up at 0.7 mol dm^{-3}, so that no ionic strength corrections need be made by the modelling program. Although the former approach is much less rigid in that it allows for an exact ionic strength to be calculated iteratively during the modelling study and correction of the constants to this ionic strength, it was not the approach chosen for this study for several reasons: Firstly, this approach requires two sets of ionic strength adjustments; one adjustment from the ionic strength at which the measurement was made to zero ionic strength using LOGK or LOGKSP, and the second adjustment from zero ionic strength to 0.7 mol dm^{-3} by the modelling program MINEQL. MINEQL makes use of an extended form of the Debye-Hückel equation as proposed by Davies [14] for ionic strength adjustments. Unfortunately the adjustments made using the Davies equation were not consistent with those made by LOGK, possibly due to the fact that the former equation is only valid over small ranges of ionic strengths (up to 0.02 mol dm^{-3}) and is therefore not suitable for the large adjustments required in this study. The latter approach of setting up the database at 0.7 mol dm^{-3}, requires only one set of ionic strength adjustments from the ionic strength at which the

measurement was made to the ionic strength of seawater. Since a fair number of the constants are available at ionic strengths close to 0.7 mol dm^{-3}, these adjustments could be made over a smaller range, using the empirical techniques employed by LOGK, thus minimising the error associated with ionic strength adjustments.

The form of the model used in this study is given in Appendix A, in the input format required by the program MINEQL. The model of inorganic speciation consists of reactions for the formation of 435 soluble complexes and 54 potential solids from the 32 inorganic components given in table 2.2. Extension of the model to include organic equilibria, which will be discussed in section 2.5, required data for the formation of a further 110 soluble complexes, bringing the total to 520 soluble species including the protonated ligands. It should be noted that solubility considerations have been entered as formation reactions for the solid phases and hydroxyl species given in terms of the proton equilibria. These conventions can best be illustrated by the following example for the input of the solid calcium hydroxide, from the solubility reaction

$$Ca(OH)_2\,(s) = Ca^{2+} + 2OH^-$$

which has a value for log K of -4.32 (0.7 mol dm^{-3}).
Written as a formation reaction for the solid this gives

$$Ca^{2+} + 2OH^- = Ca(OH)_2\,(s)$$

with a formation constant of log K = 4.32 at 0.7 mol dm^{-3}. Addition of twice the ionic product of water gives the input required by MINEQL, namely

$$Ca^{2+} + 2H_2O = Ca(OH)_2\,(s) + 2H^+$$

with a value for log K of -23.22 (0.7 mol dm^{-3}).

Modelling is an ongoing process and refinements and adjustments continually need to be made as new constants are added and considerations of kinetic factors require modification of existing constants. Thus at no time can this work really be considered as complete.

2.4 VALIDATION OF THE MODEL

2.4.1 Validation of the model with respect to pH

The model was validated by comparison of computed results for several different systems with experimentally determined results reported in the literature. The pH of seawater is the result of a web of interactions between all of the major ions as well as the carbonate and carbon dioxide equilibria. Thus agreement between experimentally determined pH values and those predicted by the model, involves not only validation of the acid base equilibria but also of the ionic interactions of the major ions.

The interpretation of operational pH measurements raises the fundamental theoretical problem of the immeasurability of a single ion activity [80]. In seawater the problem is compounded by the high ionic strength of the medium. As a result three different pH scales are presently used for the determination of seawater pH. They are the National Bureau of Standards pH scale (NBS) [81] and the constant ionic medium pH scales proposed by Hansson [82] and by Bates and Makaskill [81]. (Prior to 1960, several measurements of seawater pH were made on the Sørenson pH scale). Since the measurement of pH in seawater is of great importance to any speciation study, a brief discussion on the various pH scales in use will be given.

2.4.1.1 The NBS pH Scale

The notional definition of pH in terms of hydrogen ion activity

$$pH = -\log a_H$$

cannot contribute directly to practical measurements because of the immeasurability of a single ion activity. Instead an operational approach is adopted whereby the measurements in the sample solutions are compared to those made in a standard buffer of assigned pH(S) in the operational cell :

$$\text{Reference electrode} \mid \text{KCI } (< 3.5\ \text{M}) \mid \text{X or S} \mid H_2 \text{ electrode}$$

The value of pH (X) is given by:

$$pH(X) = pH(S) + \{E(S) - E(X)\} / gT - \{E(JS) - E(JX)\} / gT$$

where $g = (R/F)\ln 10$ and E(S) and E(X) are the emfs in the standard and test solutions respectively and E(JS) and E(JX) are the liquid junction potentials for the standard and test solutions.

The NBS pH scale is defined by five dilute NBS buffers [81] of assigned pH. If the sample and standard buffer differ in ionic strength as in the case of seawater, then the change in liquid junction potential (the residual liquid junction potential) manifests itself in an error in the determined pH(X) value making any interpretation of the pH in terms of hydrogen ion activity difficult. However since seawater of fixed salinity is effectively a constant ionic strength medium the liquid junction potential and ion activity coefficients are stabilised and the uncertainty in interpretation of the measured pH(NBS) in terms of an approximate hydrogen ion activity is a constant. For seawater at 25°C the following approximate relationship holds:

$$pH_{NBS} = pa_H - 0.076 \quad \text{...2.19}$$

where pH_{NBS} refers to the measured pH on the NBS scale and pa_H refers to the immeasurable hydrogen ion activity [83].

2.4.1.2 The total hydrogen ion pH scale

Hansson [82] defined a pH scale for seawater based on the total hydrogen ion concentration

$$pH(SWS) = - \log m_H^T$$

where m_H^T is the sum of the free and complexed hydrogen ion molalities in the seawater sample (mol kg^{-1} water).

The pH(SWS) scale is based on synthetic seawater containing sulphate and buffered with 2-amino-2-(hydroxymethyl)-1,3-propanediol. Owing to the formation of the hydrogen sulphate ion , the total hydrogen ion concentration (m_H^T) differs from the concentration of free uncomplexed hydrogen ion (m_H). Thus

$$pH_t = pm_H - \log (1 + \beta_{HSO4} M_{SO4})$$

where β_{HSO4} is the protonation constant for SO_4^{2-} and M_{SO4} is the molality of SO_4^{2-} in solution.

For seawater of 35‰ salinity at 25°C this gives the following approximate relationship:

$$pH_t = pM_H - 0.130 \quad \text{...2.20}$$

By matching the ionic strength of the saline standards to seawater the residual liquid junction potential is minimised. However, proper application of this scale requires a knowledge of the effects of pressure and temperature on the protonation constants of hydrogen sulphate.

2.4.1.3 The free hydrogen ion pH scale

Proposed by Bates and Makaskill, the third pH scale for seawater is based on the concentration of the free uncomplexed hydrogen ions :

$$pm_H = -\log(m_H)$$

where m_H is the molality of free hydrogen ion in seawater.

Standardization of electrodes is against synthetic, sulphate free seawater buffers containing hydrochloric acid (0.01 mol kg^{-1}). Although the problem of residual liquid junction potential is minimized, interpretation of measurements in terms of free hydrogen ion molalities is complicated by the formation of HCl^+ ion pairs [83]. The activity coefficient of hydrogen ions in seawater has been estimated to be approximately 0.83. Based on this, an approximate relationship between measurements made on this scale and the activity of hydrogen ions can be made [83]:

$$pm_H = pa_H - 0.080 \qquad \text{...2.21}$$

2.4.1.4 The determination of calculated pH(NBS) and pH(SWS) values from the results of the model.

The program MINEQL can be used to determine a value for the molar concentration of the free hydrogen ion in seawater. From this it is possible to calculate an approximate value for $pH(NBS)^{calc}$ and $pH(SWS)^{calc}$, using the approximations given in equations 2.19 and 2.20 and a guessed value for the activity coefficient of H^+, namely 0.83 [83]. Comparison of the calculated pH values with those determined experimentally can be used to validate the model. According to the results of the model, the concentration of free hydrogen ions is 6.76×10^{-9} mol dm^{-3}, which on the molality scale gives a value of 6.88×10^{-9} mol kg^{-1}. Substitution into equation 2.20 results in an approximate value of $pH(SWS)^{calc}$ of 8.03. This compares favourably with the value for pH(SWS) measured in natural seawater of pH(SWS) = 7.795 [82]. By using a guessed value of the activity coefficient of H^+ in seawater, together with equation 2.19, an approximate value for $pH(NBS)^{calc}$ = 8.16 can be calculated from the hydrogen ion concentration determined in the model. The experimentally measured value of pH(NBS) in natural seawater is 7.954 [82]. Bearing in mind that the above calculations are only approximations, the agreement between experimentally determined pH values and those calculated from the modelling results is sufficiently good for the purposes of this modelling study.

2.4.2 Considerations on the precipitation of calcium and magnesium carbonates from surface seawater

Initial modelling studies showed the carbonates dolomite, magnesite and calcite to precipitate from surface seawater. In a discussion on the solubility of these carbonates, however, Ahrland [60] points out that neither dolomite nor magnesite are precipitated from surface seawater, despite their occurrence in sedimentary rock. Since considerable care has been taken in selecting solubility products for

these solids relevant to seawater conditions, the discrepancy between our initial modelling results and the report by Ahrland must be due to some other factors playing a role. In order to solve this apparent anomaly further research into the literature was required.

The precipitation of dolomite from seawater provides a good example of a chemical phase whose solubility is determined by kinetic rather than thermodynamic constraints. Even though surface seawater is several times supersaturated with respect to dolomite [85] it does not precipitate. The main reason that has been given for this is that very precise Ca-Mg ordering is required for its formation [86]. In addition a high concentration of sulphate ions such as is found in seawater is also known to inhibit dolomite precipitation.

The observation that magnesite does not precipitate from seawater has also been attributed to kinetic factors. The hydration energy for the magnesium ion is about 20% greater than that of the calcium ion, which when combined with the low activity of free carbonate ions in seawater disfavours precipitation of magnesium rich carbonates over calcium rich carbonates since very few carbonate ions have sufficient kinetic energy to penetrate the hydration barrier of magnesium [86].

In trying to incorporate these kinetic effects into the model the above points suggest that the solubility of dolomite and magnesite should not be based on the thermodynamic constraints which would be applied in the model. Thus in order to reflect more closely the situation in real seawater, the solubility products of dolomite and magnesite have been removed from the database.

A comparison of the solubility products of calcite and aragonite under seawater conditions (4.46×10^{-7} and 7.41×10^{-7} respectively) would lead one to conclude that calcium carbonate should precipitate as the thermodynamically more stable (less

soluble) phase, calcite. Studies by several investigators [71 and references therein] have however shown that the presence of dissolved magnesium favours the precipitation of calcium carbonate as aragonite rather than calcite from supersaturated seawater and other magnesium rich solutions. Two hypotheses have been advanced to explain the inhibiting effect of magnesium on calcite crystal growth. They are:

1) Mg^{2+} acts as a surface poison [85] by being adsorbed as hydrated ions on active growth sites, and thereby inhibiting the spread of monomolecular steps on the calcite crystal surface.

2) Incorporation of magnesium into the growing calcite crystal to such an extent that the solubility is markedly increased [71] is the main reason for its inhibition of calcite precipitation

Results of experiments by Berner on the precipitation of calcite from magnesium-free seawater to which varying amounts of magnesium have been added show that magnesium does not act as a true surface poison, since at low magnesium concentrations little or no crystal growth inhibition occurs. The importance of the Mg^{2+} / Ca^{2+} ratio in the experiments however, does suggest that it may act as a simple surface poison by competing with calcium for surface sites and that its effectiveness in seawater is due to the high Mg^{2+} / Ca^{2+} ratio of five to one. A test of the second hypothesis that magnesium incorporation into the growing calcite crystal to form magnesium calcite results in an appreciable increase in solubility is provided by the experiments of Berner [71] on the seeded precipitation of aragonite and calcite from seawater. Analysis of precipitates from seawater on pure synthetic calcite seeds shows that the precipitated calcite contains 7 to 10% $MgCO_3$. The magnesium calcites have enhanced solubility relative to pure calcite. As a result of magnesium uptake, Berner concluded that the minimum degree of supersaturation

necessary to precipitate calcite inorganically from seawater is generally greater than that which exists in the open ocean. The most stable calcium carbonate phases in seawater are aragonite and magnesium calcite containing between two and seven percent $MgCO_3$.

Dissolved magnesium is not readily adsorbed on to the surface of aragonite, nor is it taken up to any extent into the aragonite crystal lattice. Nevertheless, results of experiments carried out by Berner showed that aragonite crystals precipitated from seawater but only during extended precipitation runs (10-15 hours) when an appreciable mass of the aragonite seed had been used initially.

In order to take account of the kinetic effects discussed above, namely that the precipitation of aragonite from seawater is kinetically more favourable than that of calcite owing to the presence of magnesium in seawater, the calcite solubility constant was removed from the database allowing calcium carbonate solubility to be determined by aragonite.

2.4.3 Considerations of the redox approach

For the purpose of validating the model with respect to the redox equilibria, initially it was the intention to compare computed with measured redox potentials. Operational measurements of seawater redox levels, however, generally do not yield results which are amenable to interpretation of a 'true' redox potential since the electrodes are likely to reflect the redox level of one couple only, or the measured value is a mixed potential of several couples making it difficult to interpret quantitatively [74]. This is illustrated by the wide range of Eh measurements reported for seawater samples and the still intensive debate over a pE value of seawater in terms of an acceptable indicator redox couple which reflects precisely the electron condition in the water [75, 76, 77]. Baas-Becking [87] has proposed an

average Eh for surface seawater of +400 mV, but this value cannot be explained in terms of a controlling redox couple such as the oxygen-water or oxygen-peroxide couples proposed by Sillén [76] and Breck [77] respectively for aerated surface seawater.

Thus, not being able to rely on an experimentally determined Eh measurement against which our model could be validated, it was decided to compare the general speciation pattern obtained from the model with experimental measurements of the analytical free ion concentrations reported in the literature.

For the purposes of this study the model has been set up at the pE value set by the oxygen-water couple as well as at the pE value suggested by Breck [77] for the redox level set by the oxygen-peroxide couple. Results obtained for the distribution of the metals manganese, copper and iron between their redox states at the two different pE levels were then compared with experimentally determined concentrations reported in the literature of these elements in order to determine which proposed redox couple might best reflect the situation in seawater. The results of these two models will be discussed in more detail in chapter 3.

2.5 EXTENTION OF THE MODEL TO INCLUDE ORGANICS

There has been considerable controversy over the importance of natural organic compounds in complexation of metals in seawater. The existence of metal organic complexes has been postulated as far back as 70 years ago to explain several observations such as the apparent supersaturation of ferric ions in seawater (Harvey 1928 in [88]), the fact that added organic sequestring agents increase the toxicity of copper to marine algae (Gran 1931, 1953 in [88], Sunda and Guillard 1976 [9]), as well as the fact that copper can be extracted directly from seawater into chloroform [89]. It is only recently however that techniques sensitive enough to isolate and

characterise certain metal organic complexes have been able to provide proof of the existence of such complexes.

Because of the uncertainty as to the nature and existence of such complexes, several chemists interested in metal speciation in seawater have disregarded the formation of organic complexes [17, 20, 25, 90]. Others have taken account of organic speciation by modelling in the presence of compounds with rigorously known properties such as EDTA [91], NTA [92], acetic acid and glycine [26, 93], salicylic acid and 4-sulfosalicylate [28], phthalic, tartaric and citric acids [93]. Generally, models such as these cannot realistically predict the extent of metal organic binding. Strong, non-specific complexing agents such as EDTA and NTA are likely to overestimate the extent of metal organic interactions, whereas the remaining ligands, when used singly will underestimate metal organic binding by interacting only with those metals receptive to their particular donor group. Often, although model compounds are chosen to be as representative as possible, the sum of their individual properties is a poor simulation of the overall properties of polyfunctional complexants [94]. An alternative approach involves the use of average equilibrium constants which have been empirically determined with natural samples of organic material [29, 32]. A problem associated with this approach however, is that the constants are only valid for a limited range of experimental conditions and are usually dependent upon the method of determination [94].

Organic Matter in Seawater

The natural organic matter in seawater is composed of an extremely complex mixture of compounds, most of which (80%) have not yet been identified, having a wide variety of properties including the ability to act as ligands and complex trace metals [95, 96, 97]. In order to simplify the study of this complex matrix it is convenient to divide these compounds into homologous groups, usually on the basis of molecular weight [88].

The low molecular weight ligands (< 200 amu) comprise the free amino acids, fatty acids and carbohydrates which rarely form more than 20% of the dissolved organic matter. Although potentially capable of binding metal ions, these compounds are present at very low concentrations and are rapidly recycled by microorganisms making them unlikely candidates for large-scale chelation of metals in seawater [88]. They do however play an important role in the recycling of metal ions as a result of their bioavailability.

Approximately 80% of marine organic matter can be classified as high molecular weight (5×10^2 to 1×10^6 amu), macromolecular compounds of uncertain structure, of which the humic and fulvic acids form a major fraction. The distinction between humic and fulvic acids is based on an operational definition used by Rashid and King [98] whereby the humic acid fraction is defined as that part of (soil) organic matter which is extracted by alkaline solution and then precipitated upon acidification, whereas fulvic acids are alkaline soluble compounds that stay in solution upon acidification. Fractionation of the high molecular weight organics has shown the fulvic acid fraction to constitute 50-100% of organics in surface waters. Since in general these compounds are better characterised than the humic acids and have been shown to interact more strongly with metal ions [99] further discussion will centre on the chelation of trace metals by the fulvic acids in seawater.

Marine fulvic acids are structurally poorly understood, tridimensional polymers of heterogeneous structure which exhibit polyelectric behaviour for non-trace metals and contain a wide variety of functional groups with different reactivities. They are formed in situ by condensation, polymerization and partial oxidation of smaller molecules which are excreted metabolic products of organisms or which are released on the death and decomposition of organisms. In general the input of terrestrial organic substances from rivers and streams is minor compared to primary productivity in the sea [102]. As a result of the differences in the precursor

compounds from which marine fulvic acids are formed, there are several features which distinguish them from terrestrial fulvic acids. The less aromatic, more aliphatic character of marine fulvic acids results from the lack of abundant aromatic precursors such as lignin in the marine environment [100]. Typically, marine samples are characterised by a higher nitrogen content and lower oxygen content, as well as a higher H/C ratio than terrestrial samples [100, 101].

Although their overall structure is complex and poorly understood, marine fulvic acids contain reasonably consistent and simple functional groups for metal coordination, with the result that the chemical properties for different samples are very similar [61]. Characterization of fulvic acids in terms of the nature and concentration of the functional groups is a convenient means of simplifying the overall structure, to aid in determination of the nature of their association with metal ions.

In the present study, model fulvic acid compounds are constructed using the statistical approach of Murray and Linder [103] in which randomised positioning of aromatic rings and functional groups is used to generate model fulvic acids. These model fulvic acids are then scanned to identify mono-, bi- and tridentate metal binding sites in the molecule and to obtain estimates of their concentrations. For this purpose, the computer program RANDOM [103] was used, together with analytical data including elemental composition, functional group concentrations, percentage aromaticity and molecular mass of a typical marine fulvic acid sample. The data used as input for RANDOM is given in table 2.3, taken from Buffel [94] and references therein. RANDOM generates a series of randomly assigned macrocyclic structures for each fulvic acid sample, based on several simplifying assumptions (details of which can be found in reference [103]). Each structure is scanned and the types of binding sites which correspond to those of the individual ligands in figure 2.2 are counted. The output is given in terms of the proposed concentrations of each ligand (metal binding site) for that particular fulvic acid

sample. The results of the RANDOM generated model of a typical marine fulvic acid in terms of mono-, bi- and tridentate ligands are given in table 2.4. Based on these results the proposed ligands, together with their protonation and metal binding constants for the metals magnesium, copper, zinc, manganese and iron, were incorporated into the database of the speciation program MINEQL in order to determine the effect of organics on the inorganic speciation pattern.

Table 2.3: Analysis of a typical marine fulvic acid [94].

Elemental Composition(%)

C :	50.0
O :	36.9
H :	6.8
N :	6.4
S :	0.5

Structural Composition(%)

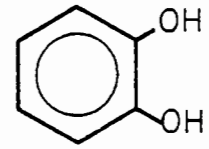
Aromatic H :	3 - 4
Aromatic C :	9

Functional Groups(meq g^{-1})

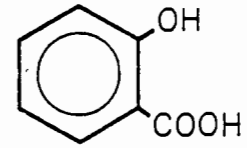
Total acidity :	2.0 - 5.5
Carboxyl :	1.0 - 4.0
Phenolic OH :	0.0 - 1.5
Alcoholic OH :	0
Carbonyl :	5.0 - 6.0

Atomic ratio H/C : 1.6

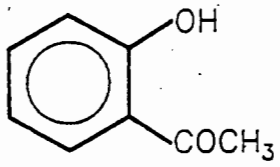
Molecular weight : 501-792 g mol^{-1}

1 

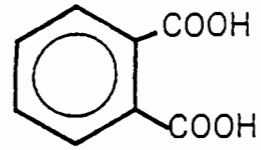
1,2–dihydroxybenzene

4 

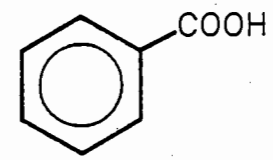
salicylic acid

5 

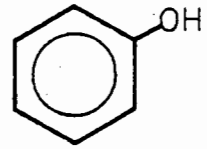
2–acetylphenol

10 

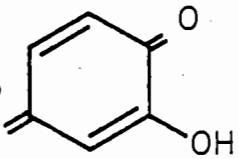
phthalic acid

15 

benzoic acid

16 

phenol

18 

hydroxy–1,4
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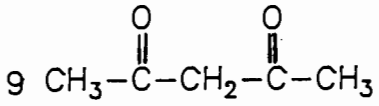
9 

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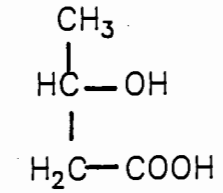
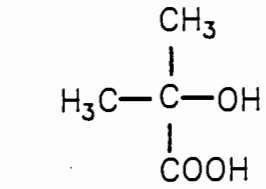
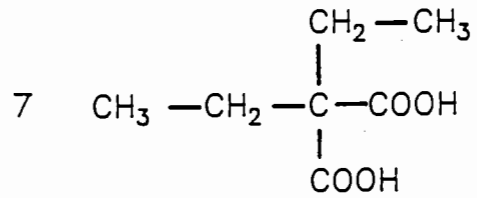
6 

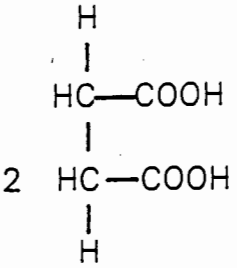
3–hydroxybutyric
acid

2 

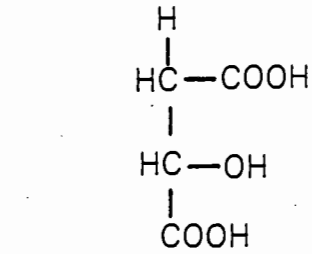
2–hydroxy–2–methyl
propionic acid

7 

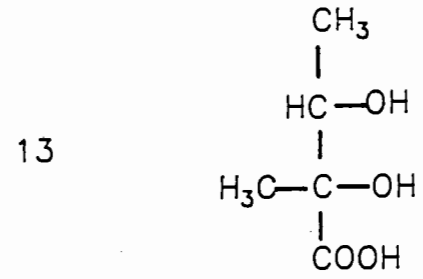
diethylmalonic acid

12 

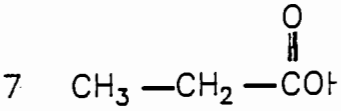
succinic acid

11 

malic acid

13 

2,3–dihydroxy–2
–methylbutyric acid

17 

propionic acid

Figure 2.2: Mono-, bi- and tridentate ligands used in RANDOM to model fulvic acid metal binding sites.

Table 2.4: Proposed concentrations of each ligand from the results of RANDOM.

Ligand	Concentration /meq dm^{-3}	Concentration for 10 $mg.dm^{-3}$ FA /meq dm^{-3}
Acetylacetone	1.13	1.13×10^{-5}
Propanoic acid	0.67	6.7×10^{-6}
Phenol	0.38	3.8×10^{-6}
Benzoic acid	0.22	2.2×10^{-6}
Salicylic acid	0.07	7×10^{-7}
3-hydroxybutyric acid	0.05	5×10^{-7}
2-acetylphenol	0.05	5×10^{-7}
2-hydroxy-2-methyl propionic acid	0.02	2×10^{-7}
Succinic acid	0.01	1×10^{-7}

CHAPTER THREE
RESULTS AND DISCUSSION

3.1 RESULTS OF THE INORGANIC SPECIATION PATTERN

For this particular study, modelling investigations were carried out following the procedure given in the flow diagram, figure 2.1. The principle aim was directed towards obtaining information on the detailed chemical speciation pattern in seawater, with particular reference to the following:

1) The inorganic speciation of the major ions Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}.

2) The inorganic speciation of biologically important elements such as Cu, Fe, Mn, Ni, Zn and of the toxic heavy metals Cd, Hg, Pb and Ag, between their oxidation states and among the inorganic ligands present.

3) The importance of organic ligands in trace metal binding, relative to the inorganic ligands, and the effect of naturally occurring organics such as fulvic acids on the inorganic speciation pattern.

An investigation into the extent of formation of ternary ligand species and polynuclear species was also carried out, based on predictions of several researchers as to their importance in multicomponent high ligand variety media such as seawater [58].

Computations have been carried out not only at the pH of seawater, pH 8.17, but also at higher and lower pHs to determine the resulting effect on coordination tendencies. In addition the speciation pattern has been computed at several different pE values, to determine the effect of redox levels on species distribution.

Where possible modelling results will be correlated with experimental results to substantiate conclusions drawn from the modelling study. Discrepancies between the speciation patterns predicted by the chemical model and experimental observations may indicate the existence of additional features which require consideration.

3.1.1 The inorganic speciation of the major ions

Results of the speciation patterns for the metals Ca^{2+}, Mg^{2+}, Sr^{2+}, K^{+} and Na^{+} versus pH are given in table 3.1. As can be seen, the major ions exist mainly in the uncomplexed free ion form (>80% for Ca^{2+}, Sr^{2+} and >90% for Mg^{2+}, K^{+} and Na^{+}), the most important ligand below a pH of 8.2 being sulphate. The speciation of Na^{+} and K^{+} remains essentially unchanged with pH, whereas that of Ca^{2+}, Mg^{2+} and Sr^{2+} changes, owing to the formation of metal carbonate complexes above pH 8.2. The most marked change being for Ca^{2+} which is 93.5% bound as the solid $CaCO_3$ at pH 9. Since dolomite and magnesite were excluded from the model (see section 2.4.2) Mg^{2+} remains in solution but the importance of the free ion form decreases with pH as the mononuclear $MgCO_3$ and dinuclear $Mg_2CO_3^{2+}$ become more important.

Table 3.1: The speciation of the major cations with pH

Cation	Species	Fraction total metal (%)						
		pH 7.0	pH 7.2	pH 7.6	pH 8.0	pH 8.2	pH 8.6	pH 9.0
Ca^{2+}	Ca^{2+}	84.8	84.8	84.8	84.4	84.1	28.1	4.5
	$CaSO_4$	15.2	15.2	15.2	15.1	15.1	5.3	0.2
	$CaCO_3$						1.1	1.1
	$CaCO_3(s)$						65.3	93.5
Mg^{2+}	Mg^{2+}	91.7	91.7	91.6	91.3	90.9	87.4	73.2
	$MgSO_4$	8.2	8.2	8.2	8.2	8.2	8.2	7.2
	$MgCO_3$						2.5	13.0
	$Mg_2CO_3^{2+}$						1.2	5.4
Sr^{2+}	Sr^{2+}	81.9	81.9	81.9	81.8	81.7	80.7	79.3
	$SrSO_4$	18.0	18.0	18.0	18.0	18.0	18.6	19.1
	$SrHCO_3^+$							1.5
K^+	K^+	97.8	97.8	97.8	97.8	97.8	97.7	97.6
	KSO_4^-	2.2	2.2	2.2	2.2	2.2	2.3	2.4
Na^+	Na^+	97.6	97.6	97.6	97.6	97.6	97.4	96.6
	$NaSO_4^-$	2.4	2.4	2.4	2.4	2.4	2.5	2.6

3.1.2 Inorganic speciation of the trace metals

The results of the speciation patterns are presented graphically in figures 3.1 to 3.11. In general the following observations can be made:

1) In the pH range considered, the ligands Cl^-, CO_3^{2-}, OH^- and to a lesser extent SO_4^{2-} are responsible for complexing the trace metals considered. NO_3^-, $B(OH)_4^-$, PO_4^{3-}, Br^-, I^- and F^- collectively bind less than 0.1% of any metal. This results in a few species being responsible for the binding of the total metal concentration.

2) The mixed ligand ternary complexes included in the model, namely the mixed halides of Cd^{2+}, Hg^{2+}, and Pb^{2+} and the hydroxy-phosphates of Cu^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+} and Pb^{2+} are insignificant, binding less than 0.01% of the total metal (table 3.2).

3) Higher order complexes of the type ML_x where x = 3,4... were found to be important for complexes involving the ligands OH^- and Cl^-.

4) Polynuclear complexes of the type M_yL_x where y, x = 2,3... were generally insignificant in cases where they were included in the model.

Some of the more important features in the computed distribution of the chemical species for each metal will be discussed below.

Table 3.2: Concentrations of ternary species, pH 8.17, pE 9.13

Metal	Ternary species	$[Ts]^*$/mol dm^{-3}	$[Tm]^\dagger$ /mol dm^{-3}
Fe(III)	$Fe(OH)(H_2PO_4)^+$	2.93×10^{-23}	8.03×10^{-9}
Fe(II)	$Fe(OH)(H_2PO_4)$	1.85×10^{-28}	2.57×10^{-18}
	$Fe(OH)(HPO_4)^-$	9.06×10^{-27}	
Cu(II)	$Cu(OH)(HPO_4)^-$	2.16×10^{-16}	4.81×10^{-11}
Zn(II)	$Zn(OH)(HPO_4)^-$	1.22×10^{-16}	5×10^{-9}
Hg(II)	$Hg(OH)(HPO_4)^-$	1.47×10^{-23}	2×10^{-11}
	$Hg(OH)(H_2PO_4)$	2.68×10^{-24}	
	$HgI_2Cl_2^{2-}$	1.39×10^{-16}	
	$HgI_2Br_2^{2-}$	5.46×10^{-19}	
	HgI_2Cl^-	1.98×10^{-15}	
	HgI_2Br^-	1.79×10^{-16}	
Pb(II)	$Pb(OH)(HPO_4)^-$	1.01×10^{-19}	5×10^{-11}
	$Pb(OH)(H_2PO_4)$	2.48×10^{-21}	
	$PbICl$	5.17×10^{-17}	
	$PbICl_2^-$	1.35×10^{-17}	
	$PbClI_2^-$	6.34×10^{-23}	
	$PbBrCl$	2.29×10^{-14}	
	$PbBr_2Cl^-$	2.06×10^{-17}	
	$PbBrCl_2^-$	7.71×10^{-15}	
Cd(II)	$CdBrI$	1.07×10^{-18}	1×10^{-10}
	$CdClNO_3$	8.20×10^{-19}	
	$CdBrI_2^-$	3.63×10^{-24}	
	$CdBr_2I^-$	1.46×10^{-21}	

* Concentration of ternary species
† Total metal concentration

3.1.2.1 The inorganic speciation of copper

In general the speciation of copper is dominated by complexation with the hydroxide and carbonate ligands, and as a result exhibits a strong pH dependency over the range of pH 7 to pH 9. (figure 3.1) Below pH 7.3 the most important species are the uncomplexed Cu^{2+} ion and the complexes $CuCl^+$, $Cu(OH)_2$ and $CuCl_2$. The fraction of the uncomplexed Cu^{2+} ion ranges from a maximum of 38.3% at pH 7 to less than 0.2% above pH 8.6. $CuCl^+$ and $CuCl_2$ decrease from 30.2% and 12.2% respectively at pH 7 to less than 0.2% above pH 8.6 and pH 8.4 respectively. In contrast to the above trends the fraction of $Cu(OH)_2$ increases rapidly from 7.3% at pH 7 to 76.8% at pH 8.4 making it by far the most important species for copper over the pH range 7 to 9. The graph for the formation of $CuOH^+$ remains essentially constant between the pH values 7.2 to 7.8, reaching a maximum of 11% at pH 7.6 and decreasing to a value of 0.6% at pH 9. The fraction of metal present as $CuCO_3$ is 1.6% at pH 7, increasing to 16.4% at pH 8.4 after which it gradually decreases to 12.4% at pH 9. A decrease in the percentage of copper bound as $Cu(OH)_2$ is accompanied by a sharp rise in the fraction of $Cu(CO_3)_2^{2-}$ between the pH values of 8.4 and 9. The complexation of copper by sulphate is very small, ranging between a maximum of 3.4% at pH 7 to 0.14% at pH 8.2. At the average seawater pH of 8.17, 74.5% of copper is present as $Cu(OH)_2$, 15.9% as $CuCO_3$, 4.8% as $Cu(OH)^+$, 1.8% as Cu^{2+}, 1.4% as $CuCl^+$, 0.9% as $Cu(CO_3)_2^{2-}$, 0.5% as $CuCl_2$ and 0.14% as $CuSO_4$.

3.1.2.2 The inorganic speciation of zinc

Zinc undergoes less complexation than copper, the dominant species over the pH range pH 7 to pH 9 being the aqua ion Zn^{2+} (figure 3.2). Other species of importance are $ZnCl^+$, $ZnCl_3^-$ and $ZnSO_4$. At pH 7 $ZnCl^+$ accounts for 29.5% of zinc, $ZnSO_4$ for 4.6% and $ZnCl_2$ for 1.6%. Between pH 7 and pH 8 the speciation

pattern remains constant. After pH 8 however, the species $ZnOH^+$ and $Zn(OH)_2$ form rapidly, at the expense of the uncomplexed Zn^{2+} and $ZnCl^+$. At pH 9, $ZnOH^+$ and $Zn(OH)_2$ account for 11.4% and 10.9% of the total zinc respectively, $ZnCl^+$ for 21.6% and Zn^{2+} for 37.8%. At the average pH of seawater (pH 8.17) the detailed speciation pattern is as follows. Zn^{2+} (50.2%), $ZnCl^+$ (28.7%), $ZnCl_3^-$ (8.8%), $ZnSO_4$ (4.5%), $ZnCl_4^{2-}$ (3.2%), $ZnOH^+$ (2.2%), $ZnCl_2$ (1.6%) and $Zn(OH)_2$ (0.4%).

3.1.2.3 The inorganic speciation of lead

The speciation of lead (figure 3.3) over the pH range pH 7 to pH 9 bears some resemblance to that of copper, in that the predominant species over the lower range of pH (pH 7 to pH 7.6) are $PbCl_2$, $PbCl^+$, $PbCl_3^-$ and the aqua ion Pb^{2+}, whereas the higher pH values above pH 7.6 are characterised by complexation with carbonate and, in this case, to a lesser extent with hydroxide ions. The relative importance of the species $PbCl_2$, $PbCl^+$ and the uncomplexed Pb^{2+} is reversed with respect to that of copper, since at pH 7, $PbCl_2$ is the dominant species (37.3%), followed by $PbCl^+$ (26.6%), $PbCl_3^-$ (26.3%) and Pb^{2+} (6.0%). The graph of the fraction of lead as $PbCl_3^-$ lies directly under that of $PbCl^+$ over the pH range pH 7 to 8.6, and thus for clarity has not been shown on the graph in figure 3.3. The fraction of metal bound as $PbCO_3$ increases from 1.5% at pH 7 to a maximum of 86.3% at pH 8.6, after which it decreases rapidly and is replaced by the species $Pb(CO_3)_2^{2-}$. At pH 9, 60.8% of lead is bound as $PbCO_3$ and 28.3% as $Pb(CO_3)_2^{2-}$. As with copper the single hydroxy species, in this case $PbOH^+$, is formed over the whole pH range, but does not complex a significant percentage of the metal. The formation of $PbOH^+$ reaches a maximum of 3.5% between pH 7.8 and pH 8. The di-hydroxy species which dominates the speciation of copper above pH 7.4, is insignificant in the speciation of lead, a fact which could possibly explain the greater importance of the carbonate complex in the speciation of lead than in that of copper

over the higher range of pH. At the average pH of seawater, pH 8.17, 73.9% of total lead is present as $PbCO_3$, 8.4% as $PbCl_2$, 6.0% as $PbCl^+$, 5.9% as $PbCl_3^-$, 3.0% as $PbOH^+$, 1.3% as Pb^{2+} and 1.0% as $Pb(CO_3)_2^{2-}$.

3.1.2.4 The inorganic speciation of iron

The speciation patterns of iron(II) (figure 3.5) and iron(III) (figure 3.4) are both dominated by single species which account for more than 80% of each metal ion over the entire pH range of pH 7 to pH 9. The predominant species are however very different. Iron(II) is present mainly as the aqua ion Fe^{2+}, which at pH 7 accounts for 92.9% of the total concentration of iron(II), the rest being divided between the species $FeSO_4$ (6.8%) and $FeOH^+$ (0.28%). The effect of pH on the speciation is most noticeable above pH 8 where a decrease in the fraction of the free ion form with pH, is almost in direct proportion to an increase in the fraction of $Fe(OH)^+$. At the average pH of seawater, pH 8.17, 89.2% of iron(II) is present as the aqua ion Fe^{2+}, 4.2% as $FeSO_4$ and 4.0% as $FeOH^+$. By pH 9, Fe^{2+} accounts for 71.3% of iron(II), $FeOH^+$ for 21.5%, $FeSO_4$ for 5.7% and $FeHCO_3^+$ for 1.4%. The fraction of metal bound as $FeSO_4$ remains essentially constant over the pH range considered.

The speciation of iron(III) is dominated by the formation of the precipitate $Fe(OH)_3$. Over the pH range pH 7 to pH 9 this species accounts for more than 88% of the total iron(III). Between pH 7 and pH 8.2 the species $Fe(OH)_2^+$ decreases steadily from a value of 10.8% at pH 7 to 0.7% at pH 8.2, while the precipitated $Fe(OH)_3$ increases from 88.6% at pH 7 to 98% at pH 8.2. Above this pH, the percentage of metal bound as $Fe(OH)_3$ decreases, and is replaced by the formation of $Fe(OH)_4^-$. The latter species accounts for 0.8% of iron(III) at pH 8.2 and increases to 5.3% at pH 9, while the fraction of $Fe(OH)_3$ decreases to a value of 94.6% at pH 9. The speciation pattern of iron(III) is made up of three complexes

involving the ligand OH^-, and the transition between the di-, tri- and tetra hydroxides results in a symmetrical distribution about the pH of seawater.

3.1.2.5 The inorganic speciation of cadmium(II), mercury(II), silver(I) and copper(I)

The speciation patterns of the metals cadmium(II) (figure 3.6), mercury(II) (figure 3.7), silver(I) (figure 3.8) and copper(I) (figure 3.9) have several features in common and as such will be discussed together. All four metal ions are strongly bound to chloride over the pH range pH 7 to pH 9 and as a result the species distributions are relatively unaffected by pH. The only other species of importance besides the chlorides are the aqua ion Cd^{2+} (constant at 2.9%) and the species $CdCO_3$ (maximum of 0.45% at pH 9) for cadmium. For mercury the species $Hg(OH)_2$ contributes a maximum of 0.3% to the total metal concentration at pH 9. The relative distributions of the chloride species of mercury and silver are similar in that their percentages increase with an increase in ligand number. That is, 82.8% of mercury(II) is bound as $HgCl_4^{2-}$, 13.5% as $HgCl_3^-$ and 3.2% as $HgCl_2$. Similarly 53.3% of silver(I) is bound as $AgCl_3^{2-}$, 45.6% by $AgCl_2^-$ and 1.1% by AgCl. Copper(I) and cadmium(II) on the other hand are both predominantly bound as the di-chloro complex which accounts for 45% of total cadmium and 88.5% of total copper(I) over the pH range considered. $CdCl^+$ binds 35.9% of cadmium and $CdCl_3^-$ 15.9% while $CuCl_3^{2-}$ binds 7.7% of copper(I) and CuCl 3.8% of copper(I).

3.1.2.6 The inorganic speciation of nickel

Between pH 7 and pH 9 nickel in seawater is mainly present as the uncomplexed Ni^{2+} and the species $NiCl^+$ (figure 3.10). Between pH 7 and pH 8, the fractions of these two species are relatively unaffected by a change in the pH, Ni^{2+} accounting for 67% of total nickel and $NiCl^+$ for 29.8%. Above pH 8 $NiOH^+$ starts to form,

decreasing the fraction of the aqua ion and to a lesser extent the fraction of $NiCl^+$. By pH 9, 63.6% of nickel is uncomplexed, 28.2% is bound as $NiCl^+$, 5.0% as $NiOH^+$ and 3.1% as $NiSO_4$. The fraction of metal present as $NiSO_4$ remains constant over the entire pH range considered. At the average pH of seawater (pH 8.17), 66.6% of nickel is uncomplexed, 29.6% is bound as $NiCl^+$, 3% as $NiSO_4$ and 0.84% as $NiOH^+$.

3.1.2.7 The inorganic speciation of manganese

Manganese occurs in seawater in the two principal oxidation states Mn^{2+} and Mn^{4+}, the latter as the solid MnO_2. Since MnO_2 is the only species of importance for the Mn^{4+} oxidation state, it was decided to include it in the speciation pattern of Mn^{2+}, instead of treating each separately as has been done in the redox speciation of copper and iron. The formation of MnO_2 from Mn^{2+} is dependent not only on the pH, but also on the pE level since it involves a change from the 2+ to the 4+ oxidation state. As a result the relative percentage distribution of individual species is affected by the redox level set in the model. The results presented here are relevant to a pH of 8.17 and a pE of 9.13 (figure 3.11). The significance of this redox level and the general effect of redox on the speciation patterns of all the metals in the model, will be discussed in more detail in section (3.2.2).

Between pH 7 and pH 8, the speciation of manganese is unaffected by a change in pH. The predominant species are the aqua ion Mn^{2+} (58.3%) and the chloride complexes $MnCl^+$ (24.7%), $MnCl_2$ (9.1%) and $MnSO_4$ (4.2%). The $MnCl_3^-$ complex binds 3.2% of total manganese, while $MnBr^+$ accounts for 0.46%. Above pH 8 some Mn^{2+} is converted to the solid MnO_2. At the pH of seawater, pH 8.17, 31.4% of manganese occurs as MnO_2, 38.8% as Mn^{2+}, 16.5% as $MnCl^+$, 6.1% as $MnCl_2$, while $MnSO_4$ and $MnCl_3^-$ account for 2.8% and 2.1% respectively.

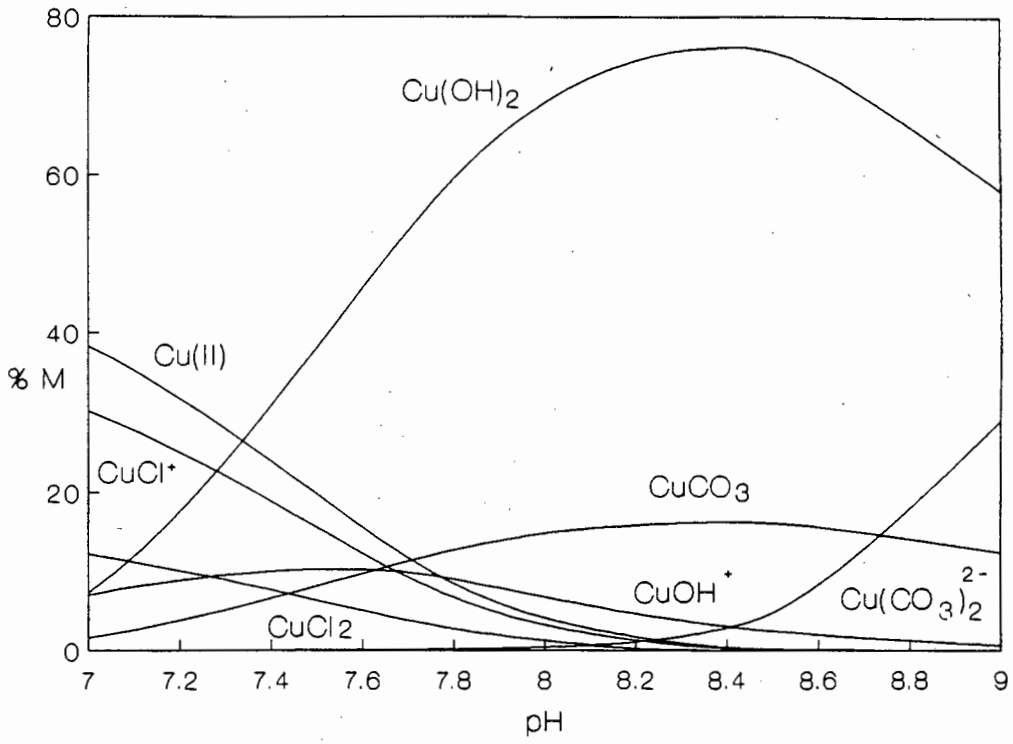


Figure 3.1: The inorganic speciation of copper(II) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

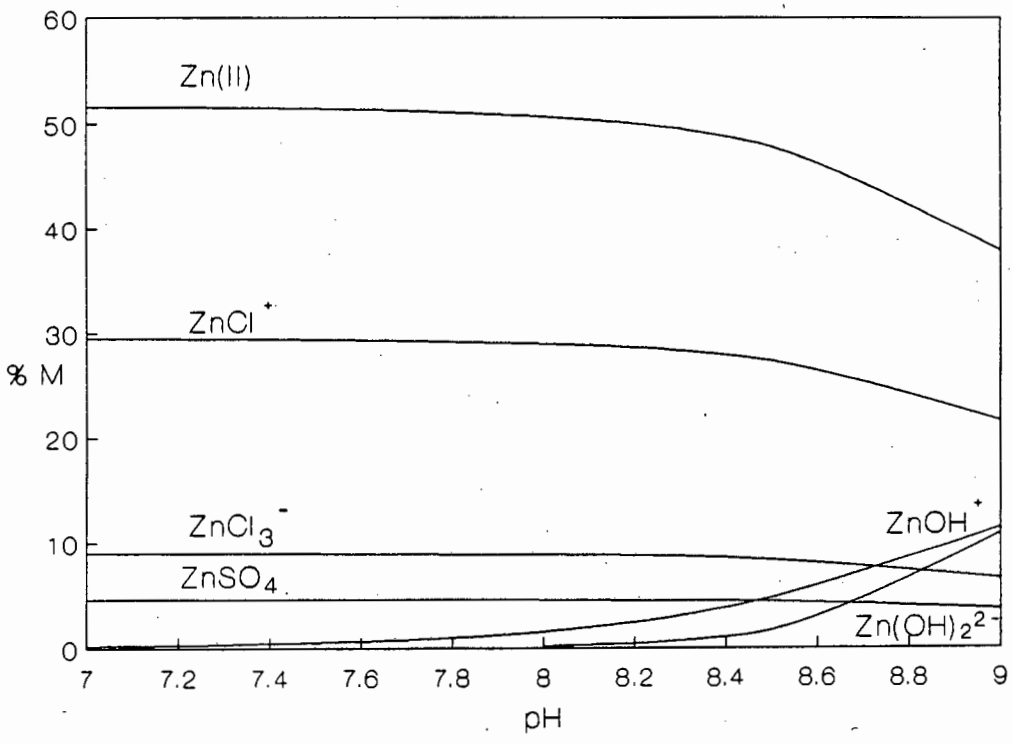


Figure 3.2: The inorganic speciation of zinc(II) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

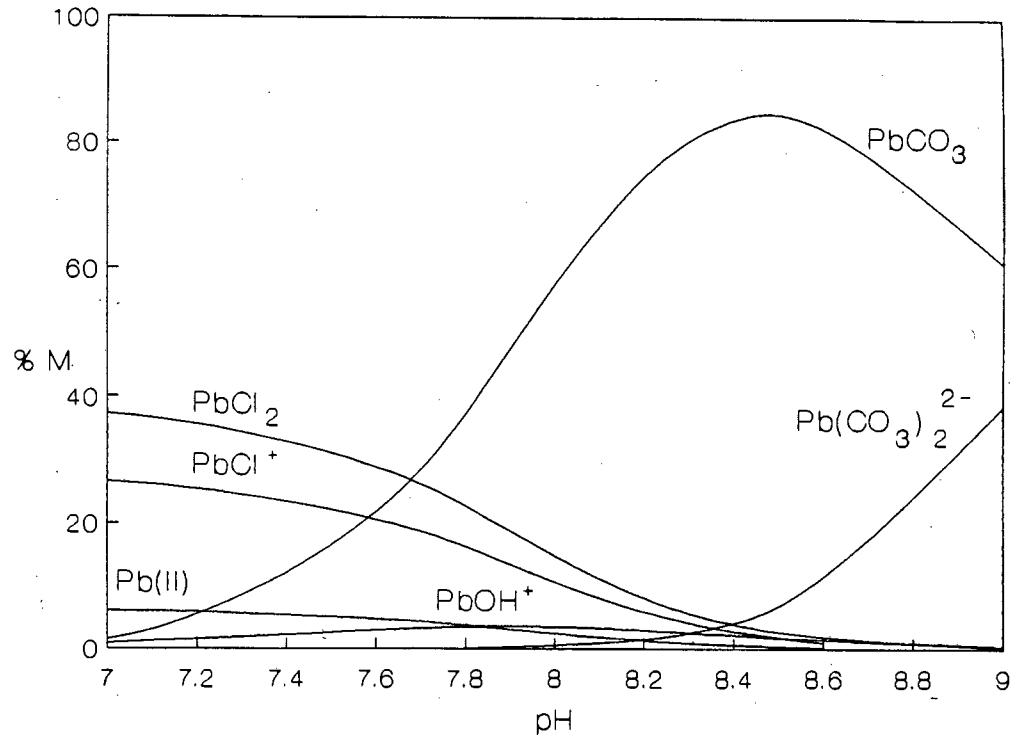


Figure 3.3: The inorganic speciation of lead(II) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

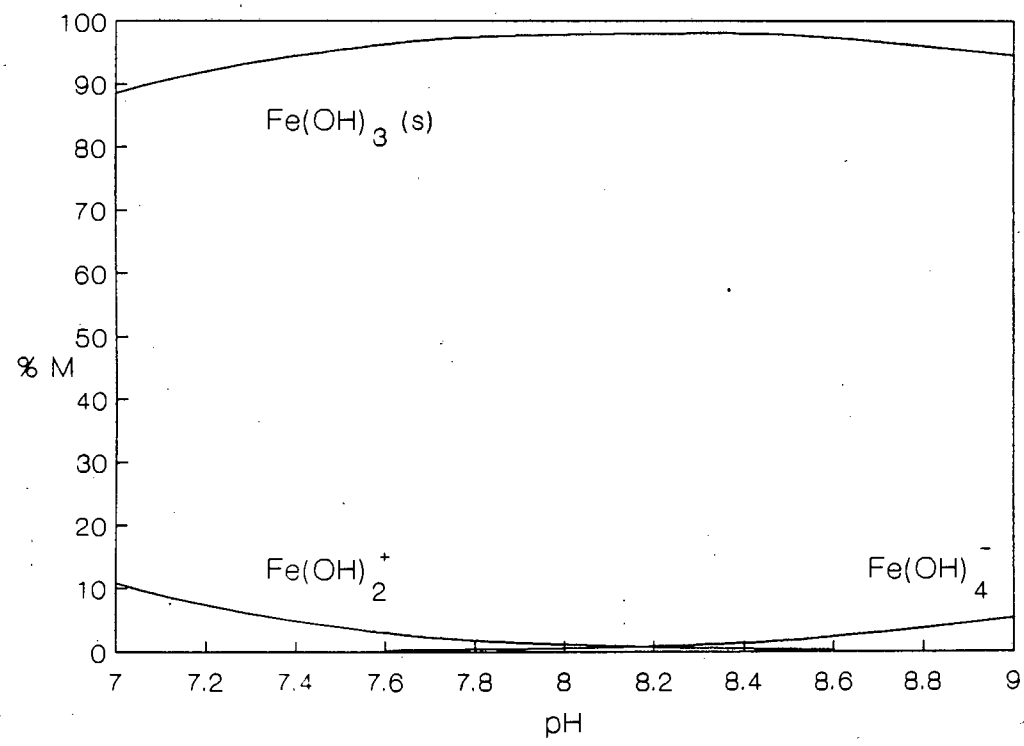


Figure 3.4: The inorganic speciation of iron(III) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

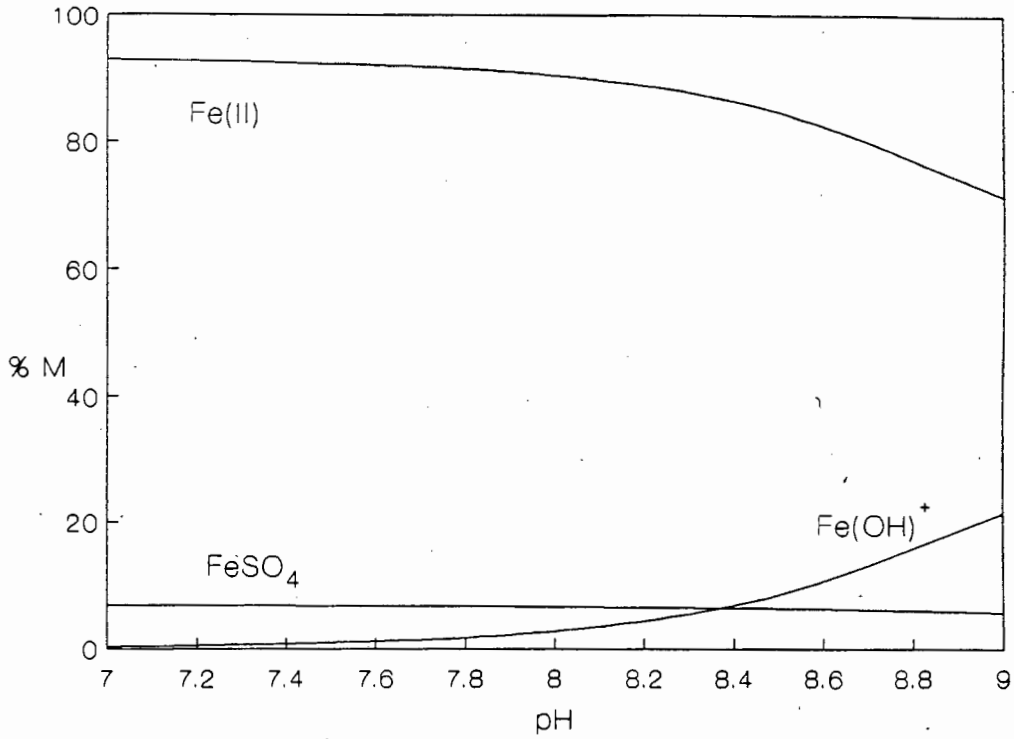


Figure 3.5: The inorganic speciation of iron(II) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

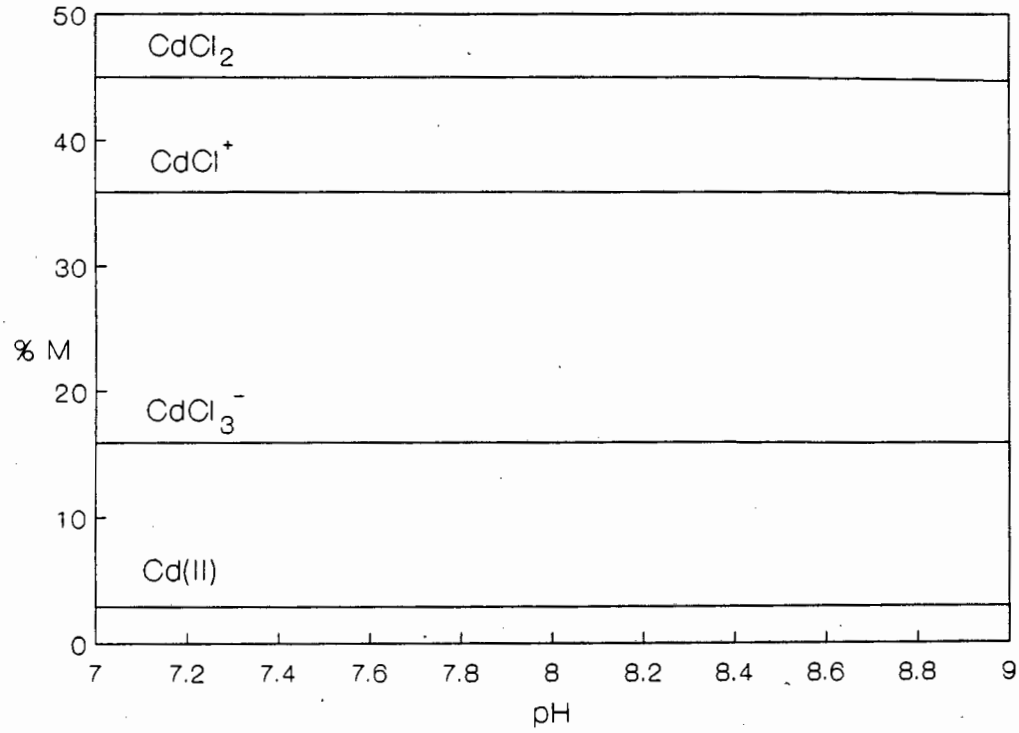


Figure 3.6: The inorganic speciation of cadmium(II) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

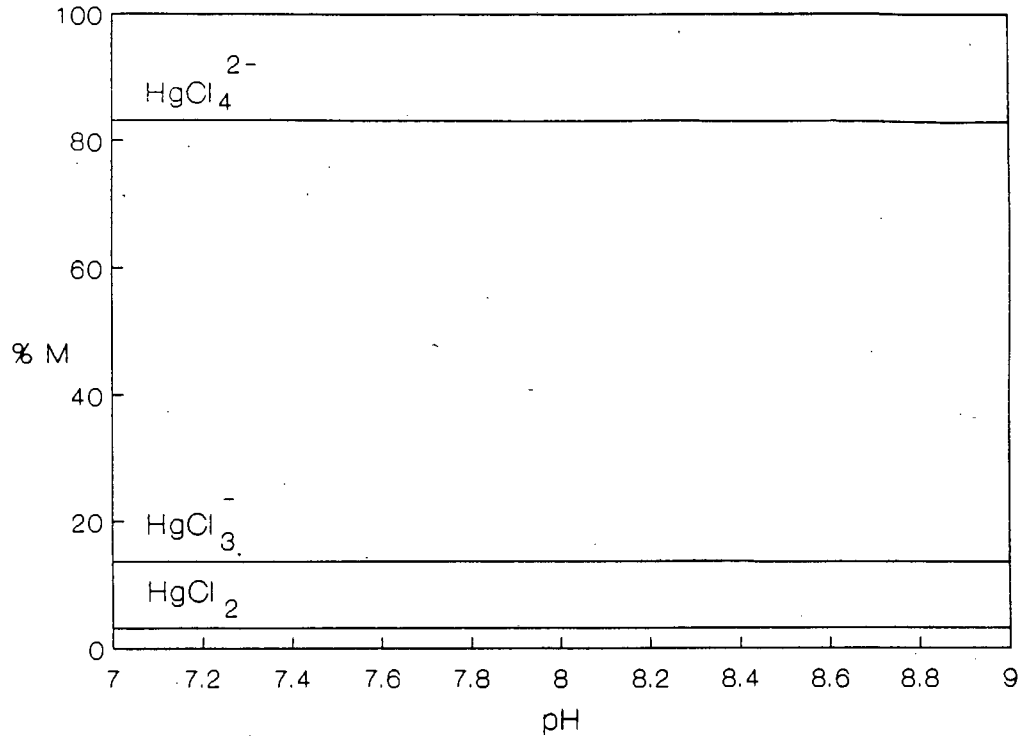


Figure 3.7: The inorganic speciation of mercury(II) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

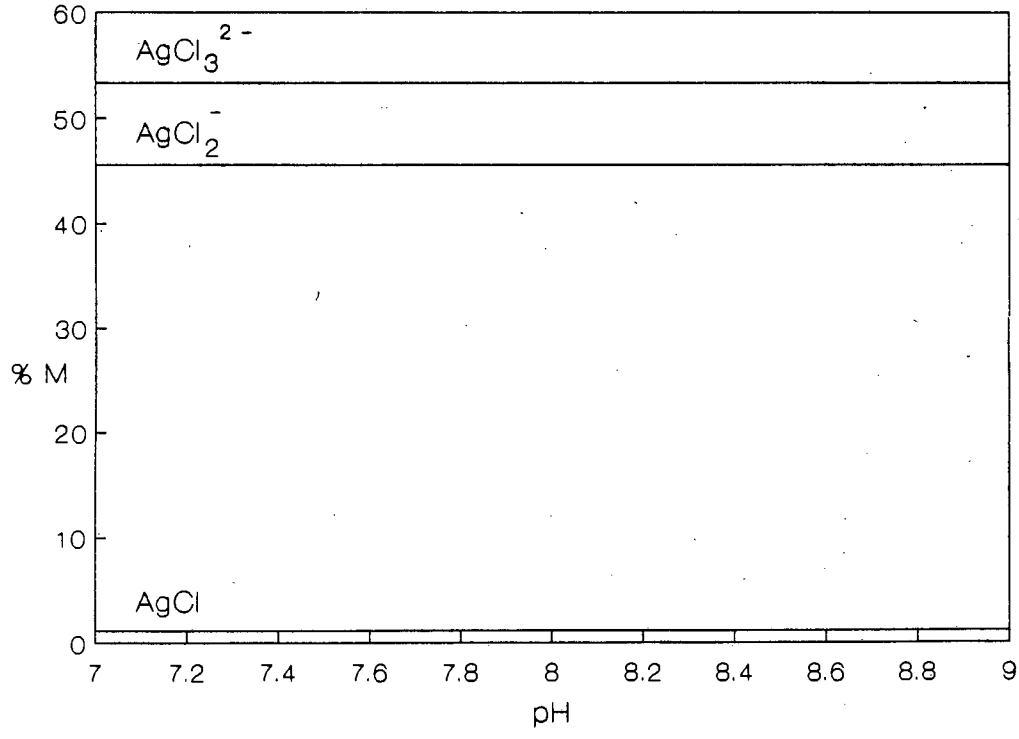


Figure 3.8: The inorganic speciation of silver(II) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

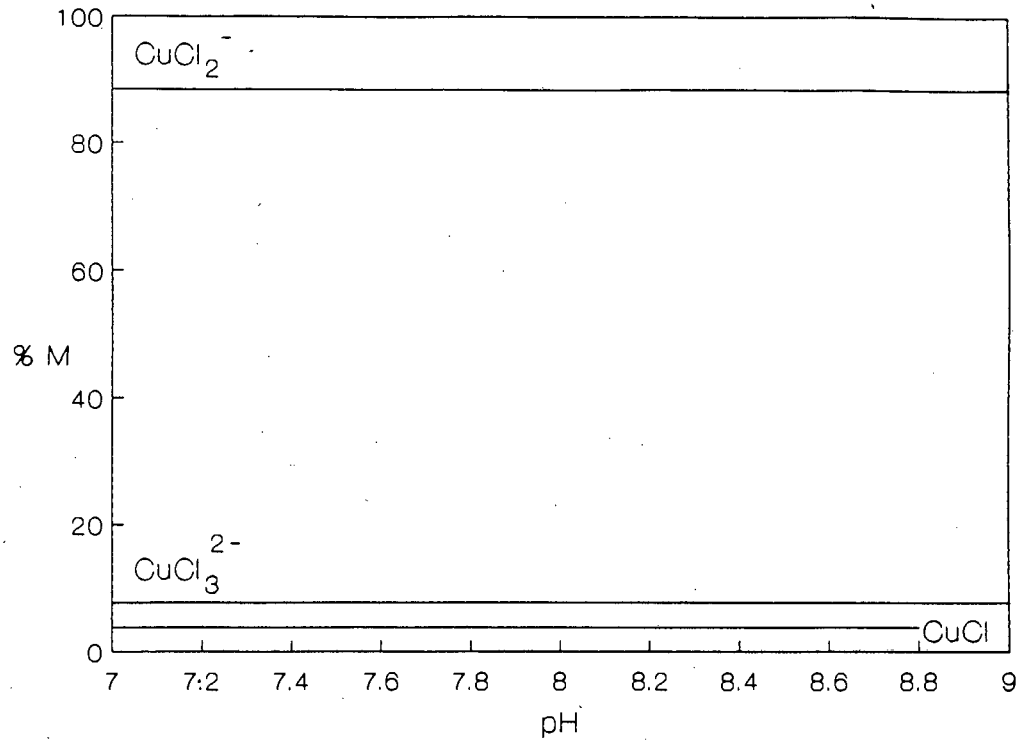


Figure 3.9: The inorganic speciation of copper(I) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

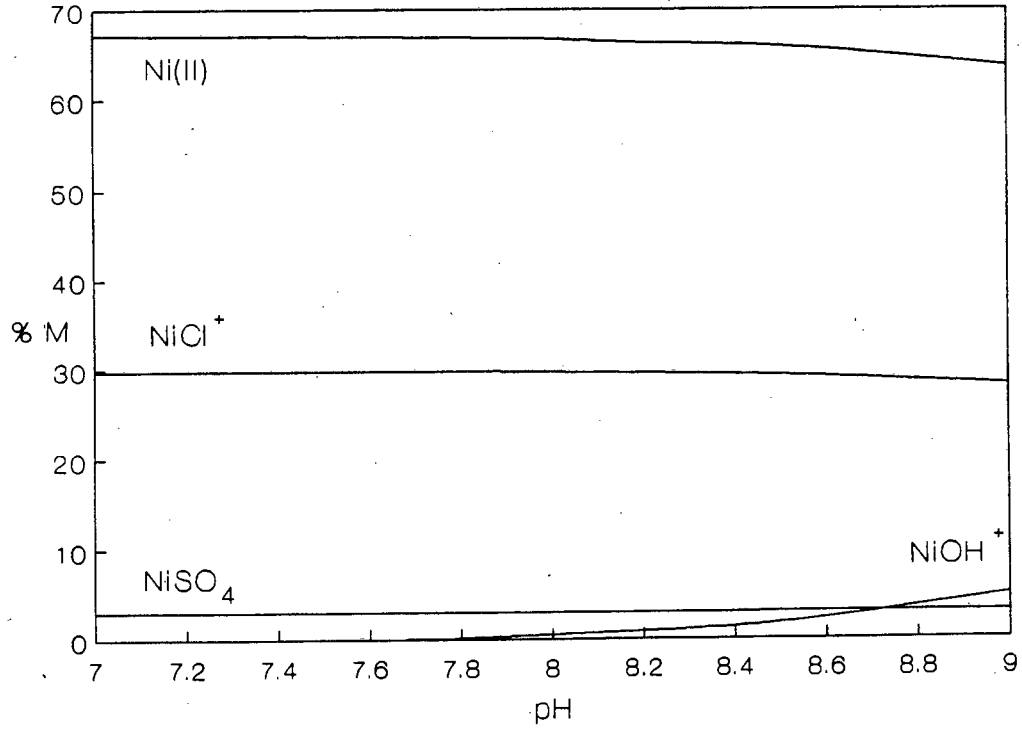


Figure 3.10: The inorganic speciation of nickel(II) as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

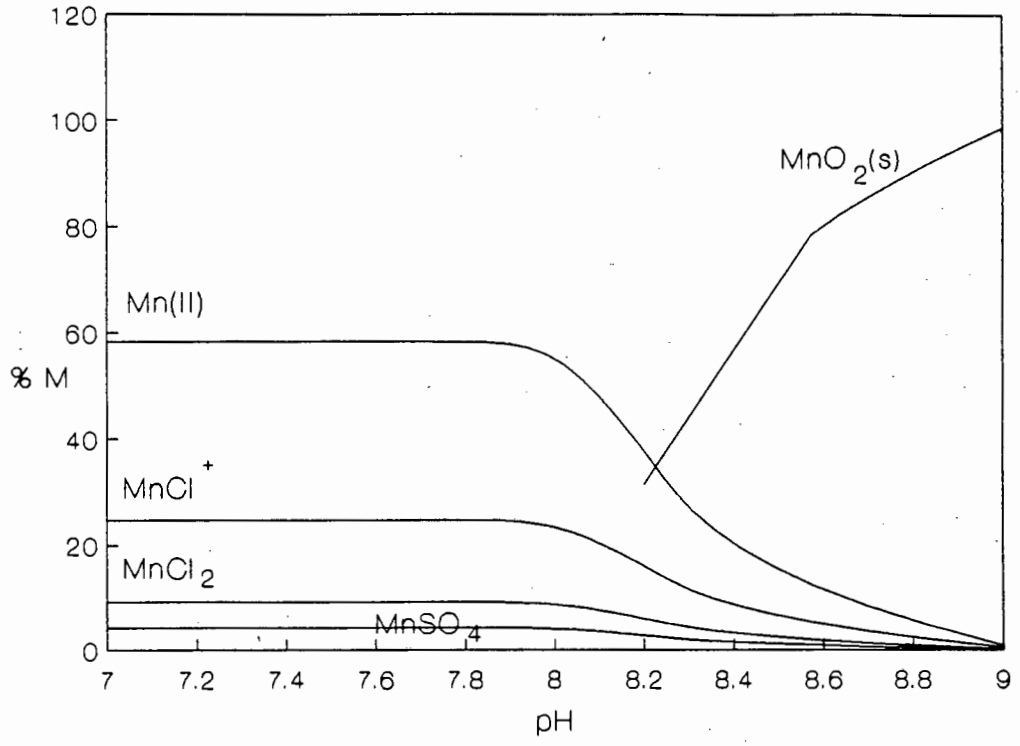


Figure 3.11: The inorganic speciation of manganese as percentage total metal versus pH (ionic strength = 0.7 mol dm^{-3}, 25°C)

3.2 DISCUSSION OF THE INORGANIC SPECIATION

The model developed in this study for the speciation of elements in seawater is based on the ion pairing concept of Bjerrum as first applied to seawater by Garrels and Thompson [17]. In general, the concept of chloride ion pairing with the major cations has not been considered in seawater models, based on the assumption that the salts of the alkali and alkaline earth chlorides are true strong electrolytes and therefore fully dissociated [18].

There is however a second school of thought which proposes that chloride does form ion pairs with the major cations in seawater. A theoretical study of the degree of ion pair formation [104] concludes that chloride ion pairs should be present in significant amounts under seawater conditions. Several independent experimental techniques have been used to measure formation constants for the ion pairs NaCl, $MgCl^+$, $CaCl^+$, KCl [105, 106, 18, 21]. Although the constants are generally small, the results obtained using different techniques appear to be in agreement. Various independent studies [18, 107, 106] have indicated that the affinity of chloride for trace metals is affected in a quantitatively predictable manner by the presence of Na^+, K^+ and Ca^{2+} ions, a fact which has been attributed to the existence of the ion pairs NaCl, $MgCl^+$ and $CaCl^+$.

For the purposes of this study, the formation of chloride ion pairs with the major cations has not been considered in the final model. Preliminary modelling studies, in which the formation of chloride ion pairs were considered showed that complexation with chloride decreases the free ion concentrations to about 63% for Ca^{2+}, Mg^{2+} and Sr^{2+} and to about 90% for K^+ and Na^+. As a result, the effective ionic strength is significantly lower than the generally accepted value of 0.7 mol dm^{-3}. Johnson and Pytkowicz [19] proposed that the effective ionic strength in seawater

is 0.53 mol dm^{-3} based on their model for the speciation of major ions, taking into account chloride ion pairing.

As stated in section 2.3.3, the database constructed in this study has been set up at 0.7 mol dm^{-3}. One disadvantage of this approach is that the program MINEQL is not able to adjust iteratively the formation constants to an effective ionic strength lower than that given in the accompanying database. As a result an estimation of the effective ionic strength is an approximation, since it is dependent upon computations which utilise formation constants relevant to 0.7 mol dm^{-3}. For what it may be worth, preliminary modelling studies in which chloride ion pairing was considered showed the effective ionic strength to be 0.58 mol dm^{-3}.

A comparison of results from preliminary studies with that of the final model showed that the presence of chloride ion pairing with the major cations may have some effect on the species distribution of the trace metals. In a model which takes into account chloride ion pairing with the major ions, the relative importance of chloride species in the trace metal speciation is on average 2 to 3% lower, while the importance of the aqua ion form increases by 2 to 3%. Metals for which the predominant species are the chlorides generally show an increase in the importance of the lower order species and a decrease in the importance of the higher order species. Further details of the results obtained in the presence of chloride ion pairs will not be given, since as stated previously such a model is a rough approximation and the differences noted in the speciation pattern may be the result of the discrepancy between the effective ionic strength of the model and the ionic strength at which the database has been set up.

As mentioned previously, the mixed ligand ternary complexes included in the model, namely the mixed halides of Cd^{2+}, Hg^{2+} and Pb^{2+} are not significant in the speciation of these metals (see table 3.2). A possible reason for this is the

difference in the abundance of the ligands chloride (5.59×10^{-1} mol dm $^{-3}$), bromide (8.6×10^{-4} mol dm^{-3}), fluoride (7.5×10^{-5} mol dm^{-3}) and iodide (5.10×10^{-7} mol dm $^{-3}$). The statistical favourability of three as to one for the formation of mixed ligand complexes over binary complexes (see section 2.2.4) is based on an equal abundance of both participating ligands, whereas in seawater the concentration of chloride ions is far higher than any of the other halides. In general, constants for the formation of the mixed chloro-halides are larger than those for the formation of the chloride equivalents, but smaller than those for the formation of the bromide or iodide equivalent species. The difference in the magnitude of the constants however is not sufficient to compensate for the difference in ligand concentrations. As a result, bis and tris chloride species are formed in preference to the mixed chloro-bromides or chloro-iodides. The latter two species are formed in preference to the bis bromides and iodide species. Similarly constants for the formation of the bromo-iodides are larger than those for the formation of the bis and tris bromides but smaller than those for the formation of the equivalent iodides. The difference in concentration between bromine and iodine however, outweighs this and the concentration of the mixed halides falls between that of the bis equivalents.

3.2.1 The effect of pH on the speciation

The speciation pattern for each metal is unique and is the result of a combination of competition reactions between ligands and hydroxide ions for metal ions and between the metal ions and hydrogen for the various ligands. In systems where the hydroxide ion competes favourably with the other ligands for the metal ion, or hydrogen ion for the ligand, a change in the pH of the model affects the resulting speciation pattern for that metal. For example, the speciation of copper(II) is strongly dependent on pH over the range pH 7 to pH 9, since hydroxide ions compete favourably with chloride ions for the metal, the fraction of copper(II) hydroxide increasing with an increase in the hydroxide ion concentration. Similarly

the importance of copper carbonate increases with pH due to a decrease in the fraction of the protonated ligand.

Cadmium(II), mercury(II), copper(I) and silver(I), on the other hand are examples of metals for which the speciation patterns are unaffected by pH, since neither hydroxide ions nor hydrogen compete effectively for the metal ions or ligands respectively over the pH range considered. The speciation patterns of nickel(II) and zinc(II) are intermediate between the above examples, the hydroxide species becoming important towards the higher pH limit.

3.2.2 The effect of the redox level on speciation

As discussed in section 2.4.3 uncertainty exists as to the redox level of surface seawater. It is generally accepted that in aerated surface waters, oxygen forms part of the dominant redox couple, the reduced form being either water, as proposed by Sillén [76] or hydrogen peroxide as proposed by Breck [77]. In order to ascertain the affect of the redox level on the speciation pattern of other redox elements such as copper, iron and manganese, modelling runs have been carried out at different levels of pH and pE, and a comparison made between results at the same pH. A comparison of the results of the speciation patterns at pH 8.17 and pE values of 8.2 and 11.97 shows that the redox level or pE has no effect on the percentage distribution of the metal species. Thus the speciation patterns in figures 3.1 to 3.11 are applicable to either redox level. An exception to this is the speciation of manganese. Formation of the solid MnO_2 requires a redox change from the Mn(II) state to the Mn(IV) state, with the result that the percentage distribution of species is redox dependent. For all metals present in more than one redox state, the concentration of each metal in a particular state is however affected by the redox level. This is illustrated in the following table of the total concentration of each metal ion in a particular redox state for two different pE levels. A pE level of 8.2

corresponds to a model in which the oxygen-peroxide couple is predominant and that of 11.97 to a model in which the oxygen-water couple predominates.

Table 3.3: The effect of pE on the total concentration of a metal in a given redox state, at pH 8.17

Redox State	pE=8.2	pE=11.97
$[Cu^{2+}]_T$	$3.23X10^{-9}$	$3.6X10^{-9}$
$[Cu^{+}]_T$	3.75×10^{-10}	$7.04X10^{-14}$
$[Fe^{3+}]_T$	$8.03X10^{-9}$	$8.03X10^{-9}$
$[Fe^{2+}]_T$	$2.19X10^{-17}$	$3.7X10^{-21}$
$[Mn^{4+}]_T$	0	$3.9X10^{-9}$
$[Mn^{2+}]_T$	$3.9X10^{-9}$	$8.4X10^{-15}$

Problems encountered by investigators in both laboratory analysis and contamination free sampling of seawater for trace metals at nanogram per litre concentrations has resulted in very few papers being published in the literature which attempt an analysis of the species distribution of elements, and which may be used to substantiate either of the above redox models. In addition, the speciation of iron is dominated by the iron(III) form, present mainly as precipitated iron(III)

hydroxide, the distribution of which is more pH dependent than redox dependent. The most useful of the three redox indicator couples considered above, is probably manganese, since the formation of the solid MnO_2 is affected by the pE level. At the pE set by the oxygen-peroxide couple, manganese dioxide does not precipitate, and the total manganese is present as dissolved species, whereas at the redox level set by the oxygen-water couple the concentration of manganese in solution is 8.4×10^{-15} and that of precipitated MnO_2 3.9×10^{-9}. In a recent publication, Nakayama et al [108] determined the inorganic species of manganese, using electrolytic concentration and chemilumincescence detection. Electrolytic concentration was used for selective separation of manganese since chemiluminescence although very sensitive, is subject to interference from other metals such as iron and cobalt. In surface seawater samples, from which particulate manganese had been filtered, the concentration of dissolved manganese was found to range from 0.5 to 4 nanomoles per litre. Analysis of unfiltered samples showed the concentrations of manganese to be higher than in filtered samples, the difference being attributed to active manganese dioxide which adsorbs onto the glassy carbon electrode. The difference between dissolved manganese and total dissolvable manganese (which includes MnO_2) ranged between 1.5×10^{-9} mol dm^{-3} and 0.04×10^{-9} mol dm^{-3} for surface seawater samples from Sagami Bay [108].

Analyses of seawater samples from the Pacific Ocean for dissolved manganese and total dissolvable manganese concentrations using graphite furnace atomic absorption spectrophotometry have been reported by Murray et al [7]. Values for surface seawater for dissolved manganese range from less than 1×10^{-9} mol dm^{-3} to 2.5×10^{-9} mol dm^{-3}. Total dissolvable manganese concentrations at the same depths are about twice as large, indicating that manganese is equally partitioned between dissolved and particulate forms.

Assuming that manganese is a suitable indicator of the redox level in seawater, modelling runs were carried out at pE values between that of the oxygen-peroxide and oxygen-water couples to determine at what pE the speciation of manganese resembled the above experimental findings. At a pH of 8.17 and a pE of 9.13, 31.4% of manganese was found to be present as MnO_2 at a concentration of 1.22 x 10^{-9} mol dm^{-3}, while the concentration of dissolved manganese is 2.68 x 10^{-9} mol dm^{-3}. The speciation pattern corresponding to this redox level, namely pE 9.13 and pH 8.17 is given in figure 3.11. A pE value of 8.2 as used in this model to estimate the redox level set by the oxygen-peroxide couple at pH 8.17, is based on the proposed concentration of peroxide in seawater as estimated by Breck [77]. If we assume that the concentration of peroxide is between 10^{-12} and 10^{-13} mol dm^{-3} instead of 10^{-11} mol dm^{-3} as suggested by Breck, then at pH 8.17, a pE value of 9.13 can be attributed to a redox level for surface seawater set by the dominant oxygen-peroxide couple.

The conclusions reached here concerning a possible redox level for surface seawater are tentative since they are based on measurements of the concentrations of only one redox couple, and the assumption that this couple is in equilibrium with other redox couples and therefore a suitable indicator of redox levels in seawater. Until such time as reliable measurements for other redox indicators or for Eh values in seawater are available it is not possible to substantiate these conclusions further.

3.3 THE USE OF RANDOM IN THE SELECTION OF MODEL LIGANDS

The approach used in this modelling study to determine the importance of metal organic binding is different to that used by other workers who have also used model compounds to simulate natural organics (see section 2.5). The use of weaker, more specific complexing agents than EDTA [91] or NTA [92] as model compounds for

natural organics is felt to be a more realistic approach, which would give a better representation of the true importance of metal organic interactions in seawater (see discussion section 2.5). The program RANDOM provides a link between the model compounds, their relative concentrations in the model and the composition of a real fulvic acid from the marine environment, thus narrowing the discrepancy between the overall properties of the model compounds and the bulk properties of the fulvic acid. The importance of the role played by RANDOM in linking the model compounds to data from a fulvic acid sample, is illustrated by a comparison of the different models generated for a soil fulvic acid and a marine fulvic acid. Linder and Murray [103] applied the program to a well characterised soil fulvic acid sample with the following results. The percentage aromaticity of the sample has a marked effect not only on the relative importance of aromatic and aliphatic ligands but also on the relative importance of ligands within these two groups. Typically in soil fulvic acids, 48% of carbon is bound in aromatic moeities. As a result, in the model fulvic acid aromatic ligands are present in higher concentrations than aliphatic ligands. The predominant aromatic binding sites are the bidentate ligands phthalate and salicylate while benzoic acid and phenol are also present in high concentrations. The order of abundance among the aliphatic ligands is 2-hydroxy-2-methylpropanoic acid followed by 3-hydroxybutyric acid and propanoic acid. In contrast to this, marine fulvics are characterised by a 9% aromatic carbon content with the result that aliphatic model compounds are present in higher proportions than aromatics. As can be seen from the results in table 2.4, acetylacetone and propanoic acid are the most abundant ligands followed by phenol, benzoic acid and salicylic acid. Phthalic acid is not present in the model for marine fulvic acid and succinic acid is not important in either fulvic acid model.

Although models to date have provided a fair amount of insight into the importance of metal organic binding there are several factors which still need to be considered. The first is that current models do not take into account the conformational effects

of the fulvic acid on the metal binding sites. Changes in conformation resulting from electrostatic attraction and repulsion of neighbouring groups may markedly affect the metal affinity of a given group for a metal, thus making the complexation constant a function of the extent of cation complexation (loading),the pH and the ionic strength. Moreover conformations assumed by the macromolecule may prevent diketone groups from assuming a planar conformation, thus preventing enolization and metal chelation [103]. A second factor is that binding between fulvic acids and metals has been assumed to be through discrete sites on the fulvic acid, since very little is known about the actual chemical bonds or physical interaction. It is possible however that the fulvic acid behaves as a macrocyclic compound towards the metal ions, entrapping them in hydrophilic cavities [101] thus increasing the complexing capacity of the organic ligands. Another factor of importance which has not been considered in the present model is the binding potential of nitrogen and sulphur containing functional groups. Although oxygen containing functional groups have been almost universally implicated in metal binding by fulvics, the higher concentration of nitrogen and sulphur in marine fulvic acids compared with terrestrial fulvic acids may contribute substantially to their ability to complex metals.

3.4 RESULTS OF THE EFFECT OF FULVIC ACID ON THE INORGANIC SPECIATION PATTERN.

The results of the speciation patterns for the trace metals Cu^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} and Pb^{2+} at a pH of 8.17 and varying concentrations of organic ligands (between 10 mg dm^{-3} and 1000 mg dm^{-3}) are represented graphically in figures 3.12 to 3.16. Although the average concentration of humic substances in seawater is less than 10 mg dm^{-3} [94], computations have been carried out at a range of organic ligand concentrations in order to determine the resulting effect on coordination tendencies. For all metals except manganese, the graphs of percentage metal versus

concentration of fulvic acid are relevant to all pE values between pE 8.2 (oxygen-peroxide couple) and 11.7 (oxygen-water couple). The results for manganese however are specific to a pE value of 9.13, as has been discussed in section 3.2.2. Some of the more important features in computed distributions of the chemical species for each metal will now be discussed.

3.4.1 The effect of fulvic acid on the inorganic speciation of copper

The organic ligands representative of fulvic acids in seawater have a marked effect on the speciation of copper (see figure 3.12) even at fulvic acid concentrations of 10 mg dm^{-3}. At pH 8.17, in the absence of organics, the principal copper species are $Cu(OH)_2$ (74.5%), $CuCO_3$ (15.9%) and CuOH (4.8%). At a fulvic acid concentration of 2 mg dm^{-3}, 73.1% of copper is bound by acetylacetone as Cu-ACAC, 2.2% as Cu-$(ACAC)_2$, 18.4% as $Cu(OH)_2$, 3.9% as $CuCO_3$ and 1.2% as CuOH. The fraction of Cu-ACAC increases to a maximum of 82.7% at a fulvic acid concentration of 5 mg dm^{-3} after which it decreases to 39.6% at 100 mg dm^{-3}, being replaced by $Cu(ACAC)_2$ which increases sharply from 6.3% at 5 mg dm^{-3} to 60.1% at 100 mg dm^{-3}. At a fulvic acid concentration of 1000 mg dm^{-3} copper is 100% bound to organic ligands, 93.9% as $Cu(ACAC)_2$ and 6.1% as Cu-ACAC. Binding of copper by the ligands salicylic acid (SAL), propanoic acid (PROP), 3-hydroxybutyric acid (3-HBA), benzoic acid (BENZ), 2-acetylphenol (2ACPH) and 3-hydroxy-2-methylpropanoic acid (3HMP) does occur but the concentrations of the species are very small and decrease with increasing fulvic acid concentration. The affinity of copper for the organic ligands decreases in the order ACAC > ACPH > PROP > SAL > 2HMP > BENZ > 3HBA.

3.4.2 The effect of fulvic acid on the organic speciation of manganese

At pH 8.17 in the absence of organics, manganese has the following speciation: Mn^{2+} (38.3%), $MnSO_4$ (2.8%), $MnCl^+$ (16.5%), $MnCl_2$ (6.1%), $MnCl_3^-$ (2.1%), MnO_2 (31.4%). At a fulvic acid concentration of 10 mg dm^{-3} 1.3% of manganese is bound as Mn-ACAC, which forms at the expense of the solid MnO_2 (30.1%). As the concentration of fulvic acid increases so more manganese is sequestered by ACAC, decreasing the percentage solid MnO_2. At 100 mg dm^{-3} of fulvic acid Mn-ACAC binds 12.9% of manganese and MnO_2 18.5% whereas at 1000 mg dm^{-3} 66.2% of manganese is bound by Mn-ACAC and MnO_2 does not precipitate. The concentrations of the other species are also affected: Mn^{2+} (19.6%), $MnSO_4$ (1.4%), $MnCl^+$ (8.3%), $MnCl_2$ (3.1%) and $MnCl_3^-$ (1.1%) (see figure 3.13). Binding of manganese to the ligands BENZ, 3HMP, 2ACPH and SAL does occur but the concentrations of the complexes are small (<0.01%). The affinity of manganese for these ligands decreases in the above order. Formation constants for the binding of manganese to phenol, PROP and 3HBA were not available for inclusion in the database. Although the effect of organic ligands on the inorganic speciation pattern of manganese is not as pronounced as for copper, they are of significance as they serve to increase the solubility of the metal.

3.4.3 The effect of fulvic acid on the inorganic speciation of iron

The inorganic speciation of iron(III) (figure 3.4) is unaffected by the presence of organic ligands even at a fulvic acid concentration of 1000 mg dm^{-3}. The complexation of iron(II) with organics (figure 3.14) is, on the other hand significant even at a fulvic acid concentration of 10 mg dm^{-3}. In the absence of organics 89.2% of iron(II) is present as the aqua ion, 6.5% as $FeSO_4$ and 4.0% as $Fe(OH)^+$, whereas at a fulvic acid concentration of 10 mg dm^{-3}, 88.9% is uncomplexed, 6.3% is $FeSO_4$ 4.0% is $FeOH^+$ and 0.37% is Fe-ACAC. As the concentration of fulvic acid

increases the percentage of Fe-ACAC increases mainly at the expense of the aqua ion. At a fulvic acid concentration of 100 mg dm^{-3}, 86% of iron(II) is uncomplexed, 6.5% is $FeSO_4$, 3.8% is $FeOH^+$ and 3.6% is Fe-ACAC and at 1000 mg dm^{-3} 27.3% of iron(II) is Fe-ACAC while the aqua ion accounts for 64.2%, $FeSO_4$ for 4.7% and $FeOH^+$ for 2.9%.

3.4.4 The effect of fulvic acid on the inorganic speciation of zinc

In the absence of organic ligands 50.2% of zinc is present as the aqua ion, 4.5% occurs as $ZnSO_4$, 28.7% as $ZnCl^+$, 1.6% as $ZnCl_2$, 8.8% as $ZnCl_3^-$, 3.2% as $ZnCl_4^{2-}$ and 2.2% as $ZnOH^+$. At 10 mg dm^{-3} of fulvic acid 0.2% of zinc occurs as Zn-ACAC, reducing the fraction of aqua ion proportionately. At 100 mg dm^{-3} 2.1% of zinc is bound as Zn-ACAC and the fractions of the sulphate and chloride species are slightly reduced as well. The speciation at 1000 mg dm^{-3} of fulvic acid is as follows: Zn^{2+} (41.3%), $ZnSO_4$ (3.7%), $ZnCl^+$ (23.6%), $ZnCl_2$ (1.3%), $ZnCl^-_3$ (7.2%), $ZnCl_4^{2-}$ (2.7%), $ZnOH^+$ (1.8%) and Zn-ACAC (17.6%) (figure 3.15). The difference in concentrations between the metal-ACAC species and the other metal organic species is not as pronounced in the case of zinc as it is for the other metals.

3.4.5 The effect of fulvic acid on the inorganic speciation of lead

Complexation of lead by the organics representative of fulvic acid (figure 3.16) is so weak that it has little effect on the inorganic speciation pattern. In the absence of organics 1.3% of lead is present as the aqua ion, 6.0% as $PbCl^+$, 8.4% as $PbCl_2$, 5.9% as $PbCl_3^-$, 3.0% as $PbOH^+$, 73.9% as $PbCO_3$ and 1.0% as $Pb(CO_3)_2^{2-}$. At a fulvic acid concentration of 1000 mg dm^{-3} 0.36% of lead is bound as Pb-ACAC and 0.12% as Pb-PROP reducing the concentrations of $PbCO_3$, $PbCl^+$ and $PbCl_2$ to 73.5%, 5.9% and 8.3% respectively. The affinity of lead for the organic ligands decreases in the order ACAC > PROP > BENZ > 3HBA. Constants for the

binding of lead to SAL, PHEN and ACPH are not available for inclusion in the database.

3.4.6 The effect of fulvic acid on the inorganic speciation of cadmium

The organic ligands have no effect on the inorganic speciation pattern of cadmium, even at fulvic acid concentrations of 1000 mg dm^{-3}.

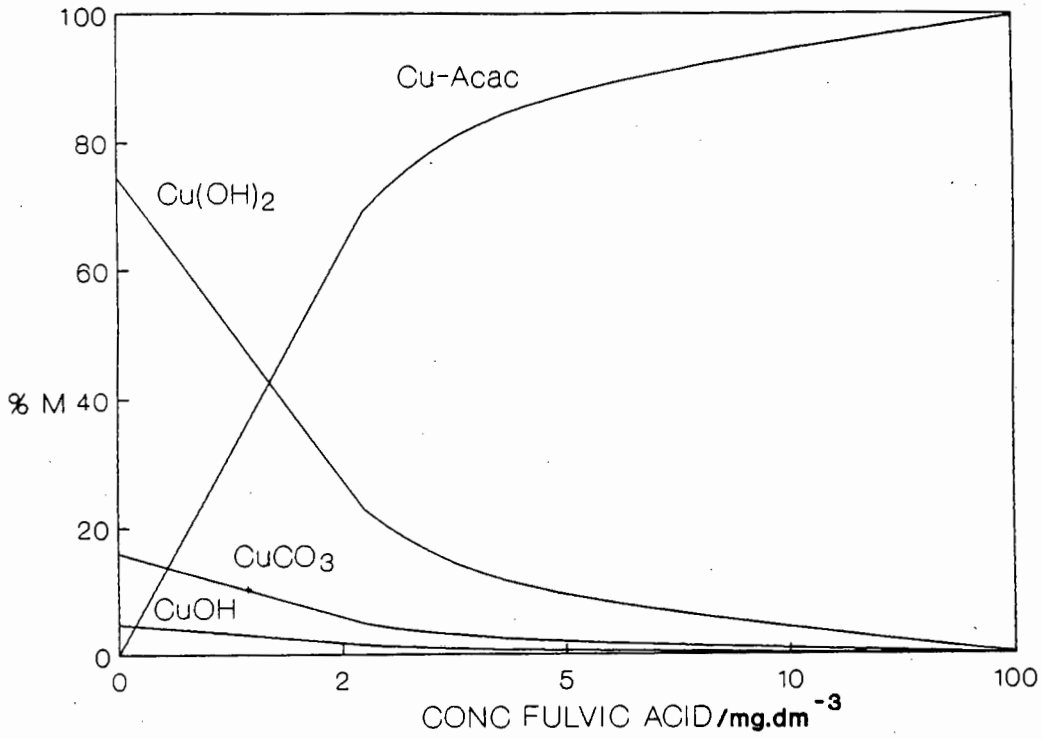


Figure 3.12: The effect of fulvic acid on the inorganic speciation of copper(II) (pH 8.17, ionic strength = 0.7 mol dm^{-3}, 25°C)

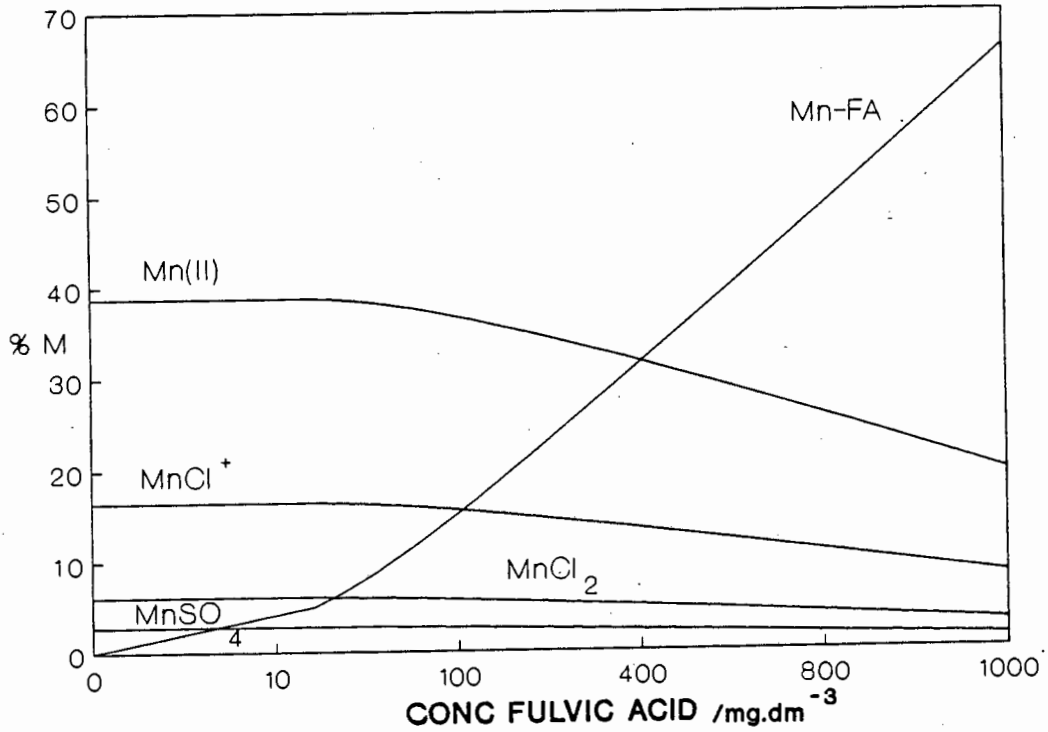


Figure 3.13: The effect of fulvic acid on the inorganic speciation of manganese (pH 8.17, ionic strength = 0.7 mol dm^{-3}, 25°C)

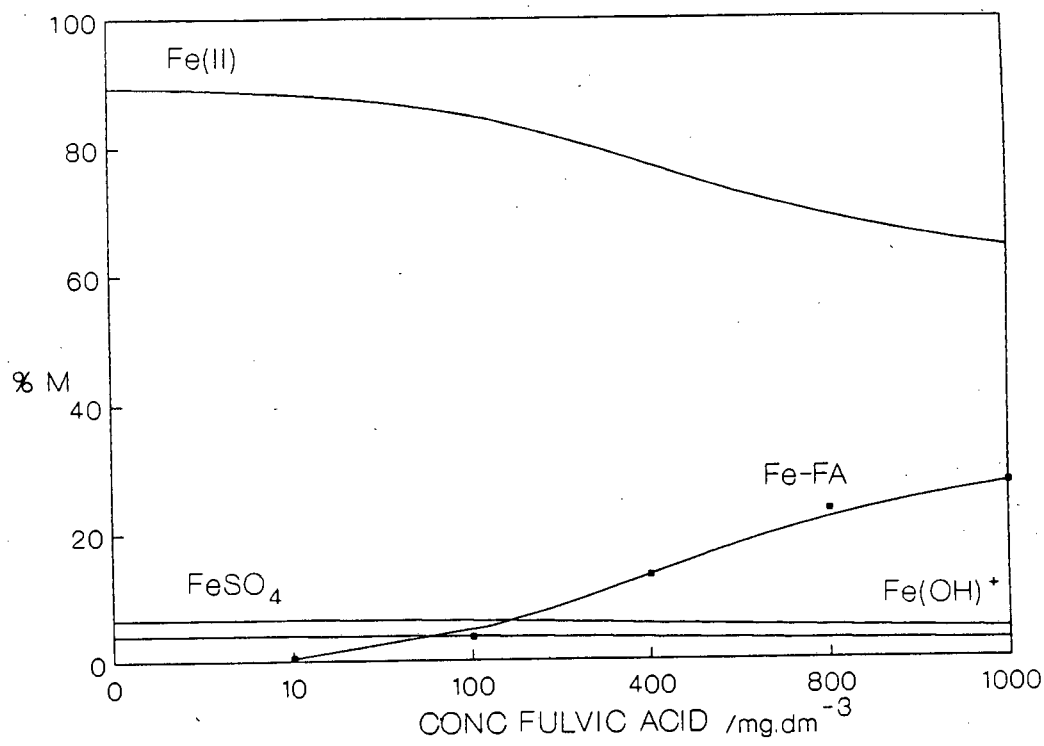


Figure 3.14: The effect of fulvic acid on the inorganic speciation of iron(II) (pH 8.17, ionic strength = 0.7 mol dm^{-3}, 25°C)

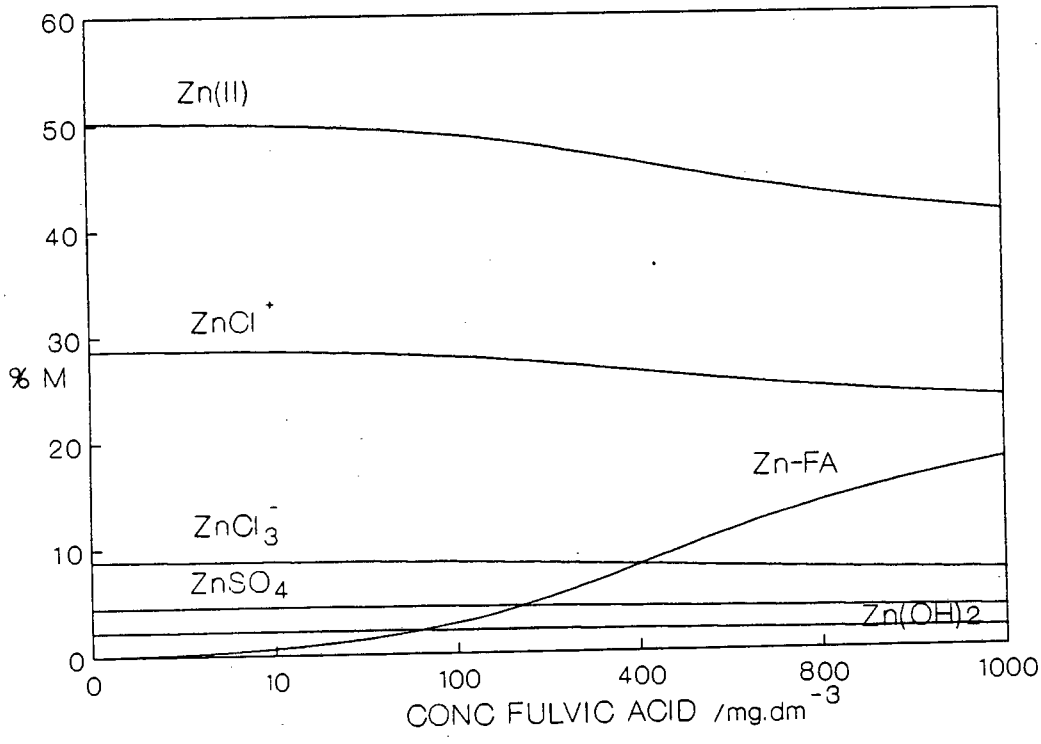


Figure 3.15: The effect of fulvic acid on the inorganic speciation of zinc (pH 8.17, ionic strength = 0.7 mol dm^{-3}, 25°C)

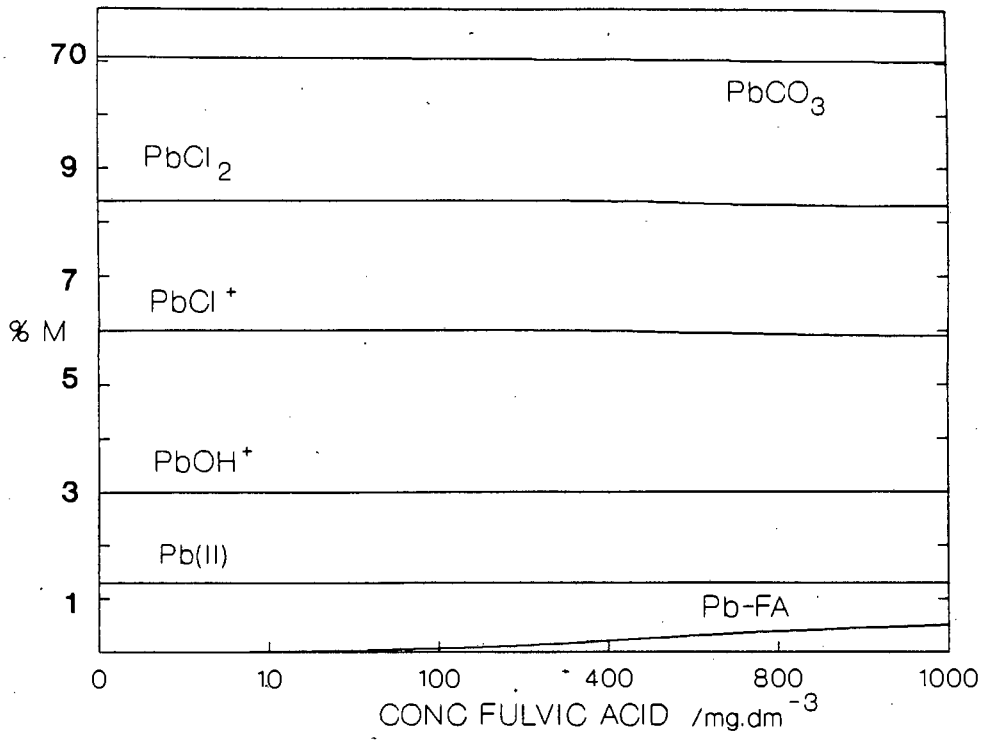


Figure 3.16: The effect of fulvic acid on the inorganic speciation of lead(II) (pH 8.17, ionic strength = 0.7 mol dm^{-3}, 25°C)

3.5 A DISCUSSION ON THE EFFECTS OF FULVIC ACID

Analysis of the results of the modelling study in which the effect of organic-metal binding on the inorganic speciation pattern was investigated showed that of the ligands used to model fulvic acid, only acetylacetone is able to compete with the inorganic ligands to any significant extent at the concentrations used. The affinity of this ligand for the metals considered decreases in the following order: Cu^{2+} > Mn^{2+} > Fe^{2+} > Zn^{2+} > Cd^{2+} > Fe^{3+}. The affinity of acetylacetone for copper(II) is so strong that at a fulvic acid concentration of 10 mg dm^{-3} 94.5% of the total copper is complexed by this ligand. Zinc is complexed by the widest range of organics, the complexes with propanoic acid, 2-acetylphenol, benzoic acid and 2-hydroxy-2-methyl propanoic acid also contributing significantly to the total metal fulvic fractions. In cases where an element can exist in two redox states the presence of fulvic acid can affect the distribution between the two states by binding preferentially to one state. According to the results of this modelling study fulvic acids should play an important part in the speciation of manganese, since by stabilising the Mn(II) state relative to the Mn(IV) state, the solubility of the metal is increased. Similarly, the speciation of iron(III) is unaffected by the presence of organics, whereas iron(II) binds significantly to acetylacetone. An increase in the concentration of fulvic acid from 10 mg dm^{-3} to 1000 mg dm^{-3} results in a 38% increase in the total concentration of iron(II) from 2.58 x 10^{-18} mol dm^{-3} to 3.57 x 10^{-18} mol dm^{-3} at pH 8.17 and pE 17.3. Similarly since the model considers the binding of copper(II) ions with organics but not that of copper(I) ions, an increase in the concentration of organics displaces the redox equilibrium towards the copper(II) oxidation state. It is unlikely that the speciation of copper(I) would be affected by binding with organic ligands, since like cadmium this metal ion is very strongly bound to chloride ions and the fraction of uncomplexed metal or other metal species is insignificant.

An analysis of the speciation patterns of the organic ligands under seawater conditions reveals a possible explanation for the generally small effect of fulvic acids on the inorganic speciation patterns of the metals at concentrations typical of seawater conditions (i.e. less than 10 mg dm^{-3} fulvic acid). In most cases, under these conditions, the ligands are almost completely bound by the metals calcium and magnesium or by hydrogen ions. Under seawater conditions 91.6% of acetylacetone occurs as Mg-ACAC and 3.3% as Ca-ACAC, the rest being made up of the protonated ligand (4.0%) and the uncomplexed ligand (1.2%). Salicylic acid is 99.9% bound as the magnesium complex. Phenol, 2-acetylphenol and 3-hydroxybutyric acid are all predominantly protonated under seawater conditions. 98.2% of phenol is protonated and 1.8% uncomplexed, 98.4% of 2-acetylphenol is protonated and 1.5% uncomplexed, while the speciation of 3-hydroxybutyric acid is as follows: 78.9% protonated, 12.4% Mg-3HBA, 8.8% Ca-3HBA. Benzoic acid, propanoic acid and 2-hydroxy-2-methylpropanoic acid are predominantly uncomplexed or bound to calcium and magnesium under seawater conditions. 92.9% of benzoic acid is uncomplexed, 5.8% is bound to magnesium and 1.3% to calcium. 84.8% of propanoic acid is uncomplexed, 13.3% is Mg-PROP and 1.9% is Ca-PROP whereas 72.3% of 2-hydroxy-2-methylpropanoic acid is uncomplexed, 22.6% is Mg-2HMP and 5.1% is Ca-2HMP. The binding of calcium and magnesium to acetylacetone, salicylic acid and to a lesser extent, 2-hydroxy-2-methylpropanoic acid, 3-hydroxybutyric acid, propanoic acid and benzoic acid results in the effective concentrations of the ligands available for binding to the transition metal ions being several orders of magnitude lower than the input concentrations. Particularly affected are the ligands acetylacetone and propanoic acid, the effective concentration of acetylacetone being reduced by 94.9% as a result of magnesium and calcium binding. Thus although the input concentration of acetylactone is much larger than that of the other ligands, its effective concentration is lower than that of either propanoic acid, phenol or benzoic acid and its importance in trace metal binding must therefore be attributed to the relative strength with which it binds

trace metals relative to hydrogen ions, compared to the three ligands of higher effective concentrations. Owing to the high concentrations of calcium and magnesium, relative to the other metals and organic ligands under seawater conditions, the fraction of these metals bound by the organic ligands is insignificant in the overall speciation of each metal. According to the results of this study, less than 2.5% of the magnesium and less than 1% of the calcium is bound by organic ligands.

In conclusion, the results of this study have shown that, with the exception of copper, inorganic speciation patterns for the trace metals are relatively unaffected by the presence of organic ligands at concentrations relative to seawater conditions. The importance of the choice of model compounds is clearly illustrated by the difference in effectiveness between acetylacetone which competes favourably with the inorganic ligands for the binding of trace metals and 2-acetylphenol which is 98.4% protonated under seawater conditions. The importance of relating the concentrations of the model compounds to the environment being simulated is clearly illustrated by the difference in speciation results at fulvic acid concentrations of 10 mg dm^{-3} and 1000 mg dm^{-3}. At levels lower than 10 mg dm^{-3} as found in surface seawater organics do not compete very effectively with inorganic ligands for the trace metals, whereas at levels of 1000 mg dm^{-3}, which may occur in sediments, with the exception of cadmium and iron(III), organics account for more than 10% of the speciation of each metal.

Based on the findings of our model, we propose that in an environment where the concentration of organics is higher, such as is found in sediments or in surface waters with dense algal blooms, or alternatively under conditions of lower calcium and magnesium concentrations such as in fresh waters, organics may form an important part of trace metal speciation.

3.6 THE DETERMINATION OF SPECIATION BY EXPERIMENTAL TECHNIQUES

The experimental determination of trace metal speciation in natural waters is a very difficult task because of the very low concentrations of these metals and the fine balance of the equilibrium in the system. Techniques available make it possible to divide each metal into operational classifications or 'boxes' based on physical behaviour of the different metal forms, with the result that speciation patterns are largely method dependent [3]. Reports in the literature on experimentally determined speciations are generally vague and often in conflict with each other, owing to the problems associated with sampling and analysis, as well as conflicting interpretations of experimental results. Examples of this can be found in a review article by Florence and Batley [95]. In this section it is intended to provide a brief summary of some of the experimental findings reported in the literature on the speciation patterns of biologically important trace metals.

3.6.1 Experimental findings on the speciation of copper, cadmium, lead, zinc and iron in seawater

There is general agreement that a significant portion of copper is associated with organic matter in seawater [91, 109, 95, 110], although there is still no precise data on the nature of these organic species. Batley and Florence [111] have used a combination of anodic stripping voltammetry (ASV) together with separation and solution techniques to provide a more comprehensive breakdown of metal species. According to their findings, 30-80% of copper in seawater is associated with organics. Up to half of this (40%) is associated with colloidal organic species such as humates and organic detritus, while the rest is present as non asv-labile organic complexes (16%). Labile metal, an operationally defined parameter includes the aqua ion, simple inorganic or organic complexes such as carbonate or citrate

complexes, together with metal associated with colloidal species such as hydrated iron(III) oxide or humic substances. Non asv-labile inorganic complexes account for approximately 23% of total copper. Sugimura *et al* [110] using selective adsorption of organic metal complexes on to XAD-2 resin concluded that 83-90% of copper is organically associated in seawater. Foster and Morris on the other hand, report only 6-40% of total copper occurring as organic complexes [111]. They determined ionic copper using the diethyldithiocarbamate method and total copper after UV-irradiation of the sample.

The experimental determination of cadmium speciation in natural waters is particularly difficult because of the low total concentration. In the absence of organic adsorbents most dissolved cadmium in seawater is present as the chloro complex. Baric and Branica and Bubic and Branica studied the ionic state of cadmium in seawater using electrochemical techniques and concluded that the principal form is $CdCl^+$ [95]. Colloidal organic matter can adsorb cadmium and alter the speciation dramatically as can be seen from the results of Batley and Florence [111]. According to their findings 75% of cadmium is associated with organic colloids or bound by asv-labile organics in seawater, the inorganic fraction comprising only 18% of total cadmium.

The chemical form of iron in all oxygenated natural waters is highly complex. Sugimura *et al* [110] were able to recover 80-90% of the dissolved iron from seawater on a hydrophobic resin (Amberlite XAD-2) and have described this fraction as "dissolved organic iron". However in a similar experiment conducted on lake water, Mantoura has shown that colloidal iron particles may be trapped within the macroreticular structure of the resin and has cautioned the use of this technique for differentiating organic from inorganic forms [88]. Florence and Batley [95] report that stabilization of the ferrous state is believed to be achieved by naturally occurring organics. Theis and Singer found that many organic compounds prevented

oxidation of Fe(II) [95]. Despite this organic protection of the iron(II) state Boyle *et al* found that less than 10% of total iron in estuary water is present as Fe(II) [95].

The chemical state of lead in seawater has not been widely investigated. The asv-speciation scheme devised by Batley and Florence [111] was applied to the speciation of lead in seawater. It was found that a high proportion of dissolved lead (40 to 80%) is associated with colloidal inorganic particles, while a smaller fraction (10 to 35%) is adsorbed onto organic colloids. Labile (ionic) lead represents 10 to 40% of the total, while molecular organic and inorganic lead complexes account for 0 to 20% and 0 to 30% respectively.

Batley and Florence [111] found that approximately 50% of zinc in surface coastal Pacific Ocean water is asv-labile and extractable by chelex-100 resin indicating the presence of simple organic and inorganic compounds not adsorbed onto colloids. Baric and Branica used polarography with a zinc amalgam electrode to investigate the possible ionic forms of zinc in seawater. Their results suggest that zinc should exist predominantly as Zn(II) with a smaller fraction of $ZnOH^+$ [95].

3.6.2 Comparison of experimental findings and modelling results

The use of computer modelling for the prediction of speciation patterns results in a more detailed account of individual species than can be obtained using experimental techniques. In general however the agreement between the speciation patterns predicted from the modelling results and the available experimental findings is fairly good thus giving some confidence in the proposed model. An important feature highlighted by the experimental results, which has not been included in the model is the consideration of adsorption of metals, ligands and complexes onto inorganic and organically coated colloids and solid particles.

The results predicted by the model for the speciation of copper are substantiated by experimental findings, which emphasise the importance of organics in copper binding. Cadmium in the absence of colloids is, according to the experimental results principally bound by chloride ions, which is in agreement with the predictions from the model. If adsorption equilibria were to be taken into account by the model it is quite feasible that a large fraction of cadmium may become colloidally associated, since 55% of the cadmium species are charged. The experimental findings on the organic protection of the iron(II) oxidation state, are in agreement with the results of our modelling study. As discussed in section 3.5 an increase in the concentration of organic ligands from 10 mg dm^{-3} to 1000 mg dm^{-3} results in a 38% increase in the concentration of ferrous iron in the modelled seawater. Experimental findings on the speciation of lead in seawater show that the speciation pattern is dominated by adsorption onto colloids. Thus the speciation pattern for lead predicted by the model does not compare very well with experimental findings. Both sets of results do however show that lead is preferentially associated with inorganics rather than organics in seawater. The experimental determination of the speciation of zinc in seawater indicates the presence of simple inorganic and organic compounds [111]. These results are in agreement with the findings from the model which predict that complexation by inorganics predominate and that humic substances (large complex organics) account for less than 1% of zinc under conditions relevant to surface seawater (i.e. modelling in the presence of fulvic acid concentrations less than 10 mg dm^{-3}). The predominance of the Zn(II) ion predicted by the model is substantiated by the experimental findings of Baric and Branica [95]. A discussion of the experimentally determined speciation pattern of manganese in seawater has been given in section 3.2.2. A comparison between the experimentally determined distribution of manganese [108] and the results of our modelling study, was made in order to predict tentatively, a redox level for surface seawater. In a recent publication Nakayama *et al* [134] state that the predominant dissolved species of manganese is the aqua ion Mn(II) and that complexation by

organics is unimportant. This supports the findings of the model, that complexation of manganese by fulvic acids accounts for 1.3% of total dissolved manganese under seawater conditions.

CHAPTER FOUR
CONCLUSION

4.1 CONCLUSION

A comprehensive discussion of the results obtained in this modelling study as well as a comparison between the speciation patterns proposed by the model and those determined from experimental results reported in the literature has been given in the preceding chapter. Thus, the purpose of this chapter is to evaluate the extent to which this study has been successful in meeting the objectives set out in chapter 1, and to point out some areas of possible future research which have arisen during the course of this study.

The primary objective of this work has been to establish a model for the chemical speciation of elements in surface seawater which would update and improve on the existing models reviewed in chapter 1. This model should serve as an analytical tool for providing further insight into the processes which control dissolution, precipitation and redox processes and coordinative interactions in surface seawater.

A major aspect of this study involved the construction of a relatively extensive database. For this purpose equilibrium constants and solubility products for roughly 580 equilibria arising from interactions of 32 inorganic components (table 2.2) and 10 organic components (table 2.4) have been selected from the critical compilations of stability constants (37, 38, 39, 41 and 63) and adjusted to an ionic strength of 0.7 mol dm^{-3}, using an extended form of the Debye-Hückel equation [51]. Thus the database constructed in this study combines the use of critical formation constants as in the model of Motekaitis and Martell [28] with the wide range of reactions covered by the database of Turner *et al* [29].

Several kinetic factors relevant to seawater conditions have been taken into account in setting up the model. These include kinetic considerations for the precipitation of calcite, aragonite, magnesite and dolomite from seawater (section 2.4.2) as well as

considerations for the distribution of metals between the redox states by the oxygen-water and oxygen-peroxide couples (section 2.4.3). A comparison was made between the computed species distribution at each of these redox levels set by the oxygen-water and oxygen-peroxide couples and experimentally determined speciation distributions reported in the literature for surface seawater. Based on the assumption that the manganese redox couple is in equilibrium with the other redox couples and that it is a suitable indicator of redox levels, it is proposed that the reduction of oxygen to peroxide is responsible for setting the redox level in seawater. Although the model of Turner *et al* [29] takes into account the existence of more than one oxidation state for certain metals, the effect of pE on the distribution between these states was not investigated, and the redox level was assumed to be set by the oxygen-water couple.

One of the principle aims of this study was directed towards obtaining information on the detailed inorganic speciation patterns for the major ions and trace metals in seawater. The findings of Johnson and Pytkowicz [18] concerning the effective lowering of the ionic strength as a result of chloride ion pairing were substantiated by preliminary modelling results (section 4.2). Further investigations are however necessary in order to determine the implications of this effect on the inorganic speciation patterns of the trace metals, particularly those predominantly bound by chloride ions.

The formation of polynuclear and mixed ligand complexes, thought to be of significance for complex solutions such as seawater, yet which have not been considered in previous models has been investigated in this study. The results of the model show that the mixed halides and the hydroxy-phosphate complexes considered, are insignificant in the speciation patterns of the metals concerned (table 3.2), thus indicating the need for further modelling studies involving other mixed ligand complexes. Polynuclear complexes were also found to be insignificant in cases where they were included in the model.

The approach used in this modelling study to determine the importance of metal organic binding is different to that used by other workers who have also used model compounds to simulate natural organics (section 2.5). The choice of model ligands used in this study is based on an analysis of a marine fulvic acid sample, the latter being used as input to the program RANDOM, which generates a model fulvic acid in terms of characteristic metal binding sites. This approach is felt to be a more realistic representation of natural organics than the use of strong, non-specific complexants such as EDTA or NTA [28] or of randomly selected groups of model compounds [93].

In general the speciation results predicted by the model compare favourably with those determined by experimental techniques. An important aspect of the experimentally determined speciation patterns which has not been taken into consideration in the model, is that of adsorption equilibria for the adsorption of metals, ligands and complexes onto colloids and solid particles. The importance of these equilibria in controlling the concentrations of trace metals and in particular the heavy metals cadmium, mercury and lead in the water column needs to be investigated in future modelling studies.

Construction of a database relevant to seawater conditions involved an extensive survey of the literature, during which it became evident that although there are numerous publications on the formation constants for carbonic acid, agreement between researchers is poor. For this reason it was decided to determine the protonation constants, and if time permitted, some of the formation constants for carbonic acid at 25°C and 0.7 mol dm^{-3}. Work on this system has been detailed in Appendix A. The protonation constants were successfully determined in sodium chloride and sodium perchlorate media. The determination of formation constants however was not very successful for reasons discussed in the Appendix.

Thus the model developed in this study has been applied successfully to the determination of the inorganic and organic speciation of major ions and trace metals in seawater. The objectives listed in chapter 1 have been accomplished with varying degrees of success and important areas for future research have been highlighted. Of foremost importance though, it is hoped that this model has contributed to a deeper understanding of the processes involved in the chemical speciation of surface seawater.

APPENDIX A
CARBONIC ACID

A1 INTRODUCTION

The task of setting up a database of the chemical reactions relevant to seawater and the formation constants describing these reactions involved an extensive survey of data published in the literature. During this process it became clear that although there were numerous publications on the formation constants for carbonic acid, the agreement between researchers was poor. Moreover very little of the work had been carried out under conditions relevant to seawater. Since the carbonate system is of particular importance to seawater, having been closely linked with the pH buffering of the oceans [112], it was decided to determine the protonation constants, and if time permitted, some of the formation constants of carbonic acid at 25°C and 0.7 mol dm^{-3} sodium chloride.

This section, section A1, aims at summarising briefly the reports in the literature on the protonation constants of carbonic acid. In the following sections a discussion will be presented on the theory behind the use of potentiometry for the determination of formation constants (section A2) and on the results and findings of our work on the carbonate system (sections A3 and A4).

The reactions involving the dissociation of carbon dioxide in water and the ionization of carbonic acid have been dealt with in section 2.3.2.4 but will be summarised briefly for convenience. They are:

$$CO_2(g) + H_2O = H_2CO_3^* \quad ...1$$

$$H_2CO_3^* = H^+ + HCO_3^- \quad ...2$$

$$HCO_3^- = H^+ + CO_3^{2-} \quad ...3$$

By convention $H_2CO_3^* = H_2CO_3^\circ + CO_2$ (aq), where the ratio $H_2CO_3^\circ : CO_2$ (aq) is about 1:650 [14]. Reactions 2 and 3 have been given in terms of the ionization of carbonic acid since this is the form of the reaction used in the literature. The speciation program MINEQL however requires constants to be expressed in terms of the formation reactions. Table A1 contains a summary of the literature values proposed for the ionization constants K_1 and K_2 together with the method of determination and the journal reference for each. All constants given in the table are relevant to 25°C; the apparent constants have been determined in artificial or natural seawater and the ionic strengths at which the stoichiometric constants have been determined are stated. The thermodynamic constants have been reported at 0.0 mol dm^{-3}. The results of the different workers, while agreeing amongst themselves in the orders of magnitude of the two ionization constants show considerable diversity in the actual values. The "apparent" dissociation constants have not been considered for inclusion in the database since they are not strictly stoichiometric constants, however it is felt that a brief discussion of these constants is of use to illustrate the wide range of interpretations of the constants K_1 and K_2 in the literature.

Buch and Lynman in Mehrbach *et al* [112] and Hansson [114] determined values for the apparent dissociation constants of carbonic acid in natural or artificial seawater. However, owing to the different expressions used for K_1 and K_2 as well as the different activity scales used, the results are not directly comparable. The constants determined by Buch are defined as:

$$K_1 = \{H^+\} [HCO_3^-]_T \; / \; \{CO_2\} \{H_2O\}$$

$$K_2 = \{H^+\} [CO_3^{2-}]_T \; / \; [HCO_3^-]_T$$

where { } represents activity and [ ] represents the total concentration of each species including such species as ion pairs with the major cations.

TABLE A1: The ionization constants of carbonic acid (K_1, K_2)

A: Thermodynamic constants

Constant (log)	Method of determination	Reference
$\log K_1 = -6.34$	potentiometry	128
$\log K_2 = -10.25$	potentiometry	128
$\log K_1 = -6.36$	conductance	128
$\log K_1 = -6.36$	conductance	129
$\log K_1 = -6.35$	potentiometry	130
$\log K_1 = -6.36$	potentiometry	131
$\log K_1 = -10.33$	potentiometry	132
$\log K_2 = -6.35$	conductivity	132

B: Stoichiometric constants at 0.7 mol dm^{-3} NaCl

Constant (log)	Method of determination	Reference
$\log K_1 = -6.001$	potentiometry	115 #
$\log K_2 = -9.54$	potentiometry	115
$\log K_1 = -5.98$ þ 0.02		38
$\log K_2 = -9.54 - 0.01$		38

C: Stoichiometric constants at 3.0 mol dm^{-3} $NaClO_4$

Constant (log)	Method of determination	Reference
$\log K_1 = -7.987$	potentiometry	116 *
$\log K_2 = -9.63$	potentiometry	116
$\log K_1 = -7.88$		116
$\log K_2 = -9.56$		116
$\log K_1 = -9.56$		38
$\log K_2 = -6.33$		38

D: Apparent constants for seawater

Constant (log)	Method of determination	Reference
$\log K_1 = -5.989$	potentiometry	Buch [112]
$\log K_2 = -8.97$	potentiometry	Buch [112]

$\log K_1 = -\ 6.00$	potentiometry	Lynman[112]
$\log K_2 = -\ 9.10$	potentiometry	Lynman [112]
$\log K_1 = -\ 6.004$	potentiometry	112
$\log K_2 = -\ 9.115$	potentiometry	112
$\log K_1 = -\ 5.857$	potentiometry	112
$\log K_2 = -\ 8.947$	potentiometry	112

: The corresponding betas are $\log \beta = 9.54$ and $\log b = 15.54$

* : The corresponding betas are $\log \beta = 9.63$ and $\log b = 17.62$

Estimation of the $\{H^+\}$ was based on an operational pH scale defined by Sørenson (see section 2.4.1) and the activity of carbon dioxide was estimated relative to an infinite dilution scale i.e. $\{CO_2\}/[CO_2]$ approaches 1 when $[CO_2]$ approaches 0 in pure water. Lynman and Mehrbach both used the same expression for the constants K_1 and K_2, namely:

$$K_1 = \{H\}\,[HCO_3^-]_T / [H_2CO_3^*]_T$$
$$K_2 = \{H\}\,[CO_3^{2-}]_T / [HCO_3^-]_T$$

Estimation of the hydrogen ion activity was based on the NBS pH scale in both cases, however since the measuring cells were calibrated on different buffers, the unknown residual liquid junction potentials contained in each set of measurements result in differing values for the constants K_1 and K_2 in each case (see section 2.4.1). Hansson obtained values for the constants K_1 and K_2 in borate-free artificial seawater. For the general reaction:

$$HA \rightleftharpoons A^- + H^+$$

he defined the dissociation constant as

$$K_H = [H^+]_T\,[A^-] / [HA]$$

Measurements were made on the seawater pH scale defined by Hansson (see section 2.4.1) based on the total concentration of hydrogen in solution.

Values for the stoichiometric ionization constants have been reported in the literature at 25°C and 0.7 mol dm^{-3} sodium chloride [115] and at 25°C, 3.0 mol dm^{-3} sodium perchlorate [116]. These constants are defined by the following equations

$$K_1 = [H^+]\,[HCO_3^-] / [H_2CO_3^*]$$
$$K_2 = [H^+]\,[CO_3^{2-}] / [HCO_3^-]$$

The results of these workers will be discussed together with the results from this study in section A4.

A2 THEORY

In an aqueous solution of metal ions (M), ligands (L), and protons (H), numerous different chemical equilibria are set up for the formation of a variety of different chemical complexes. The amount of reaction product at equilibrium is determined by the stability, equilibrium or formation constant of each species as well as the relative total concentration of the species present. Thus for the general case which takes into account the formation of protonated, hydroxy polynuclear and oligonuclear complexes according to the following reaction:

$$pM + qL + rH = M_pL_qH_r$$

the overall or cumulative thermodynamic stability constant may be defined as:

$$^{T}\beta_{pqr} = \{M_pL_qH_r\} / \{M\}^p \{L\}^q \{H\}^r \qquad ...A1$$

where p,q,r are the stoichiometric coefficients of the metal, ligand and proton respectively and { } denotes activities. The formation of hydroxy complexes is denoted by negative values of r.

It is conventional to express equilibria in terms of formation reactions of the complexes from their components as opposed to dissociation reactions. As a result equilibrium constants are referred to as formation or stability constants and more specifically as protonation constants for reactions between ligands and protons and complexation constants for the formation of complexes containing metal ions, ligands (and protons). Most equilibria are studied in aqueous solutions in which the cationic species are solvated by water molecules eg. H_3O^+, $Co(H_2O)_6^{2+}$ and complexation reactions should be regarded as the displacement by the ligand of an

unknown number of solvent molecules on binding with the metal. As such, the activity of water should appear in the expression of the thermodynamic formation constant [117]. It is usually assumed that water is at a constant concentration, which is, moreover its standard state. In dilute solutions under standard conditions of temperature and pressure it is assumed that the activity of water is near unity and remains constant on keeping the activity coefficient unchanged by means of a supporting electrolyte. As such its inclusion in the expression of the thermodynamic formation constant is unnecessary.

The use of equation A1 requires a knowledge of the activities of single ion species such as M^+, L^- and H^+. However, since physical techniques are not able to measure single-ion activities but only activity products of the cationic and anionic species present [118], it is more convenient to express formation constants in terms of the concentrations of the reactants and products. The activity or effective concentration of a species is related to its actual concentration by an activity coefficient

$$a = \gamma \times c$$

where c is the concentration in mol dm^{-3}, γ is the molar activity coefficient and a is the activity of the species.

Thus the stoichiometric formation constant in terms of concentrations is given by

$$\beta_{pqr} = [M_pL_qH_r] / [M]^p [L]^q [H]^r$$

and is related to the thermodynamic formation constant by the equation

$$^T\beta_{pqr} = \beta_{pqr} \times Q$$

where Q is the quotient of the activity coefficients for the reactants and products

$$Q = \gamma_{MpLqHr} / \gamma_M^p \gamma_L^q \gamma_H^r$$

As the titration proceeds the concentrations of reactants and products change, thus changing the ionic strength of the solution

$$I = \tfrac{1}{2} \Sigma C_i Z_i^2$$

From, for example, an extended form of the Debye-Hückel equation:

$$\lg \gamma = - Az^2 I^{1/2} / (1 + B\text{å}I^{1/2}) + CI$$

it can be seen that a change in the ionic strength affects the activity coefficients which in turn affects Q. For a meaningful determination of the formation constant i.e. in which β_{pqr} remains constant throughout the course of the titration it is necessary to maintain a constant ionic strength by means of an inert background electrolyte, the concentration of which is usually several orders of magnitude larger than that of the reactants. The stability constant measured is thus only applicable to the ionic strength (and medium) in which it has been determined.

It is generally accepted that in cases where more than one ligand is able to coordinate to a metal ion, complex formation occurs in a stepwise manner, each step being described by a stepwise formation constant. Thus the general reaction

$$ML_{n-1} + L \rightleftharpoons ML_n$$

can be described by the formation constant

$${}^{T}K_n = \{ML_n\} / \{ML_{n-1}\} \{L\}$$

This in turn is related to the thermodynamic overall formation constant by the expression

$$^{T}\beta_n = \prod_{j=1}^{n} {}^{T}K_j$$

In summary, the types and concentrations of complexes which form are determined by the total concentrations of M, L and H as well as by the formation constants which in turn are temperature and ionic strength dependent.

A useful means of linking experimentally determined parameters (such as total and/or free concentrations of M, L and H) with equilibrium constants, for the purpose of solving the latter, is via secondary concentration variables such as Z_H and Z_M. The function Z_H is defined as the average number of protons bound to a ligand:

$$Z_H = \frac{T_H - [H] + Kw\,[H]^{-1}}{T_L} = \frac{\sum_{o}^{J} j[H]^j \beta_{0ij}}{\sum_{o} [H]^j \beta_{0ij}}$$

It is dependent on the free hydrogen ion concentration only, being independent of T_H and T_L. A plot of Z_H versus pH can be used to determine the protonation constant of the ligand.

Similarly, assuming mononuclear binary complex formation only, the function Z_M which is defined as the average number of ligands bound to a metal ion is given by the following

$$Z_M = \frac{T_L - (T_H - [H] + Kw\,[H]^{-1} / Z_H}{T_M} = \frac{\sum_{o}^{J} j[L]^j \beta_{0ij}}{\sum_{o} [L]^j \beta_{0ij}}$$

This is independent of T_M and T_L concentrations being dependent only on the free hydrogen ion concentration. A plot of Z_M versus the negative logarithm of the free ligand concentration can be used to determine the complexation constants provided the ligand protonation constants are known, having been determined under the same experimental conditions.

Potentiometric titrations involving L, M and H are usually carried out at several different T_M and T_L concentrations and different metal to ligand ratios. An overlap of formation curves for different titration conditions indicates reproducibility and precision as well as the formation of mononuclear, binary complexes only. Any deviation for titrations of different metal to ligand ratios or total concentrations is usually an indication of the presence of other complexes such as protonated or hydroxy metal ligand complexes, whereas parallel plots suggest polynuclear formation. A rough estimate of the stepwise formation constants can be obtained from the pH (and pL) values of Z_H (and Z_M) using the Bjerrum half Z-bar method [119].

Several different graphical and computational methods are available for the processing of potentiometric data in order to determine formation constants. The main computational method used here for the determination of formation constants involves solving a set of simultaneous mass balance equations at each titration point. The total concentration of each component can be expressed as a sum of the individual species together with the concentration of the uncomplexed component.

$$T_M^{calc} = [M] + [ML] + [ML_2] + ... + [MLH] + ... + [MLH_{-1}]$$

which in turn can be expressed in terms of the free concentration of the component and the stability constant

$$T_M^{calc} = \sum_{-R}^{R} \sum_{0}^{Q} \sum_{1}^{P} p[M]^p [L]^q [H]^r \beta_{pqr} \qquad ...A2$$

similarly for T_L and T_H. In real terms, T_M can be determined from the expression.

$$T_M^{real} = \frac{T_M^{init} \times V^{init}}{(V^{init} + v)}$$

where T_M^{init}, V^{init} are the initial metal concentration and volume respectively and v is the volume of titrant added.

The experimental variables determined using a hydrogen ion sensitive electrode are the activity products $a_H a_{Cl}$ or $a_H a_{ClO_4}$. The activity product can be converted to $a_H m_{Cl} \gamma_{Cl}$, m_{Cl} being separately measurable. Under ideal conditions of constant ionic strength, glass electrodes exhibit a Nernstian response such that

$$E_{cell} = E_{const} + S \log[H]$$

where S is the Nernstian slope = $RTF^{-1} \ln 10$

It is permissible to write the above equation in terms of hydrogen ion concentration since the E_{const} term incorporates not only all constant potentials but also the hydrogen ion and counter ion activity coefficients together with factors arising from these [120].

Equations A2 and A3 can be equated for each component M, L and H and together with equation A4 give rise to four simultaneous equations for each titration point. Provided that there are sufficient titration points in a titration, the above equations can be solved for various formation constants. Calibration of the glass electrodes presents several problems since the electrode response is affected by factors such as adsorption of hydrogen ions onto the glass surface or dissolution of minute amounts of glass, sensitivity to metal ions in alkaline solutions, and daily variations in the standard potential of the glass membrane. Calibration against buffer solutions is not suitable owing to the difficulty of reproducing liquid junction potentials. Thus internal calibration of the glass electrodes performed in the test solution itself is most satisfactory [120]. The program MAGEC [120] and in particular the subroutine CALIBT was used to calibrate the electrodes from strong acid strong

base titration data, and to provide an estimate of the pK_w value relevant to the background medium. The pK_w and E_{const} values for the electrodes were then used in the refinement of protonation and formation constants with the aid of the ESTA (Equilibrium Simulation for Titration Analysis) suite of programs. ESTA is a computer program library that can be used for simulating equilibrium distributions of chemical species and for the analysis of potentiometric titration data. Calculations are performed by two main program modules. The first is called the simulation module (ESTA1) which can be used to perform speciation distribution calculations (task SPEC) and to simulate titrations, make calculations with respect to the formation functions Z-bar as well as estimate formation constants from the titration data (task BETA). The second module is called the optimization module (ESTA2) and is used to determine, for one or more parameters, the "best" values based on a least squares procedure over a whole system of titrations.

The program optimises simultaneously a series of N_p parameters which may be formation constants, vessel and burette concentrations, the initial vessel volume as well as electrode intercept and slope values. Optimization proceeds by minimization of an objective function:

$$U = (N - N_p)^{-1} \sum_{n=1}^{N} N_e^{-1} \sum_{i=1}^{Ne} W_{ni} (Y_{ni}^{o} - Y_{ni}^{c})^2$$

where N = total number of experimental titration points, N_e = total number of electrodes and W_{ni} = weight of the i^{th} residual at the n^{th} point.

The sum of squares of residuals may be minimised with respect to either the emf of electrode **i** at the n^{th} titration point ($Y_{ni} = E_{ni}$) or with respect to total concentration of the electrode ion **i** at the n^{th} titration point ($Y_{ni} = T_{ni}$). (The superscripts 'o' and 'c' refer to 'observed' and 'calculated'.) A Gauss-Newton least squares method is used to minimise U and the degree of optimization is quantitatively expressed by the Hamilton R-factor which is given by

$$R = (U / \sum_{n:1}^{N} N_e^{-1} \sum_{i:1}^{Ne} W_{ni} (Y_{ni}^{o})^2)^{½} \quad \text{...A5}$$

This can be compared with the expression for R_{lim}

$$R_{lim} = (N / \sum_{n:1}^{N} N_e^{-1} \sum_{i:1}^{Ne} W_{ni} (Y_{ni}^{o})^2)^{½}$$

The proposed model is assumed to be a good representation of the experimental data if $R < R_{lim}$. The Hamilton R-factor test can be used to determine whether a significant difference exists at the α confidence level between two proposed models. If:

$$R_i/R_o < R_{p,n-p,\alpha}$$

where R_i and R_o are calculated from equation (A5), p is the number of unknown parameters, n-p is the number of degrees of freedom and α is the level of confidence,

then the alternative hypothesis H_i is not very different from the model H_o [121]. In this case the simpler model should be chosen on the basis of Ockham's razor [122].

The ESTA1 simulation module can be used to generate both 'calculated' and 'observed' formation function graphs. The observed Z-bar curves are calculated from experimental data and are independent of the formation constants proposed, whereas those of the calculated Z-bar curves are derived using the proposed betas for the model. Hence the degree of superimposability of the two plots indicates the validity of the proposed model.

A3 EXPERIMENTAL

The protonation constants for carbonic acid have been determined in both sodium chloride and sodium perchlorate background media at ionic strengths of 0.7 mol dm^{-3} and 3.0 mol dm^{-3} respectively. This required making up separate stock solutions for each set of titrations since each stock solution is made up to the appropriate ionic strength with the appropriate background electrolyte in order to maintain a 'constant' ionic medium throughout the titration.

The ligand source used was Merck 'Suprapur' anhydrous sodium carbonate (molecular weight 105.99) and was stored and weighed over P_2O_5 in order to prevent the absorption of water.

Chemicals used to make up stock solutions were all at least of analytical grade, supplied by Merck and BDH. All solutions were made up in glass distilled deionised water which had been boiled out to remove dissolved carbon dioxide. These were made up to the required ionic strength using either sodium chloride (Aristar BDH) or sodium perchlorate.

The sodium perchlorate used was supplied by Merck in the monohydrate form, however since the purity is not very high the following procedure for purification was used. A five litre stock solution of approximately 4 mol dm^{-3} sodium perchlorate was made up using glass distilled water. This was then filtered through 8.0μ millipore filter and carbon dioxide free sodium hydroxide was added to raise the pH to approximately pH 10 - 11. Hydroxides were allowed to precipitate during three days standing, and then filtered out using a 0.45μ teflon millipore filter. Perchloric acid was then added to reduce the pH to between pH 3 and pH 4, after which the solution was boiled to expel carbon dioxide. After cooling nitrogen was bubbled through the solution and the pH raised to pH 7 with the exclusion of

carbon dioxide. The solution was then standardised with respect to sodium ions using a cation exchange resin, Amberlite IR-120, in the free acid form. The sodium ions displace hydrogen ions from the column which can be collected and titrated against standardised sodium hydroxide. The technique and column were first calibrated on standard solutions of sodium chloride (Aristar BDH) and were found to be accurate to within 0.5%.

In addition to the sodium perchlorate solution, determination of constants at 3.0 mol dm^{-3} $Na[ClO_4]$ also required the preparation of standard perchloric acid solutions (0.1 mol dm^{-3}) and sodium hydroxide solutions (0.1 mol dm^{-3}). The perchloric acid was prepared from BDH AnalaR perchloric acid (71% ww) which was diluted with glass distilled water and the stock sodium perchlorate solution to the correct ionic strength and acid concentration. Standardization was carried out against borax which had been recrystallized according to the procedure given in Vogel [123]. Sodium hydroxide solutions were prepared under nitrogen from Merck titrisol ampoules and stored in polyethylene bottles protected from carbon dioxide absorption by soda lime self-indicating granules (BDH). Standardization was carried out against potassium hydrogen phthalate (Merck) and checked against the standardised perchloric acid.

The determination of protonation constants in 0.7 mol dm^{-3} NaCl medium required the preparation of hydrochloric acid solutions (0.5 mol dm^{-3}) and sodium hydroxide solutions (0.2 mol dm^{-3}) as well as a stock solution of sodium chloride (0.7 mol dm^{-3}) which was made up in glass distilled water using Aristar BDH sodium hydroxide and protected from carbon dioxide absorption by soda lime self-indicating granules. The hydrochloric acid was prepared from Merck titrisol ampoules and standardised against borax as before. The sodium hydroxide solutions were prepared as above except that the background electrolyte was different.

An attempt was made at determining the formation constants for the complexes formed between zinc and the carbonate ligand as well as between copper and carbonate. The former was carried out in 3.0 mol dm^{-3} sodium perchlorate medium and the latter in 0.7 mol dm^{-3} sodium chloride and required the additional preparation of standardized zinc perchlorate and copper chloride solutions. The zinc perchlorate solution was prepared as a primary standard from granulated zinc metal dissolved in concentrated perchloric acid (BDH AnalaR). A platinum strip was added to the solution to speed up the reaction by forming an electrochemical cell and preventing polarization of the metal surface. The copper chloride solution was prepared using Merck titrisol ampoules of copper(II) chloride solution and was standardized by complexiometric titration against EDTA, using fast sulphon black f indicator, according to the method given in Vogel. The EDTA, although made up as a primary standard from the dehydrated disodium salt, was standardized against the zinc perchlorate solution using Merck indicator buffer tablets, according to the method given in reference [124].

The proton concentrations of the metal solutions were standardized by the titration with sodium hydroxide using the method of Gran [125].

All volumetric flasks and manual piston burettes were calibrated with deionised water by weighing (allowing not only for density changes with the temperature of the water, but also for the volumetric expansion of the glass with temperature and the archimedes effect on standard weights) [79].

The titration assembly consisted of a Radiometer pH meter, PHM64 and a radiometer automatic burette ABU80, which were interfaced with a Bondwell computer to control the automatic dispencing of titrant and to record the titrant volume and emf data for each titration point. Other burettes which were used to dispense background electrolyte and acid or base were supplied by Metrohm. These

were placed on lab jacks to avoid disturbing the titration solutions during dispensing. Delivery tubes introduced into the solution and which remained in the solution for the duration of the titration were fitted with non-return valves. Two hydrogen ion sensitive glass electrodes (EA109) together with a calomel reference electrode (EA 404) in which the saturated potassium chloride solution was replaced with a saturated sodium chloride solution (Aristar) were used alternately to measure the emf. Since carbonic acid is in equilibrium with carbon dioxide and the equilibrium is pH dependent, it was necessary to modify the titration vessel used to prevent the ligand from leaving the solution as $CO_2(g)$ when the solution is acidic and to prevent $CO_2(g)$ from diffusing into the solution in the basic region of the titration. If this were to happen the requirement that T_L should be known and remain constant throughout the titration would no longer be met. A titration vessel was designed so that the volume of the closed vessel was completely occupied by the ligand solution, thereby essentially eliminating the gas phase. This necessitated the use of strong acid solutions to keep volume changes during the titration to a minimum. The usual requirements of an airtight system and a water jacket for thermostatting were also included. A diagram of the modified titration vessel used in this study is given in figure A1.

Throughout the filling of the titration vessel a carbon dioxide and oxygen free nitrogen atmosphere was maintained in the reaction vessel to prevent diffusion of carbon dioxide into the solution. The commercial high purity nitrogen was further purified by being bubbled through a purification line consisting of five wash bottles, containing the following solutions:

1. 50% (w/v) solution of KOH to remove carbon dioxide.

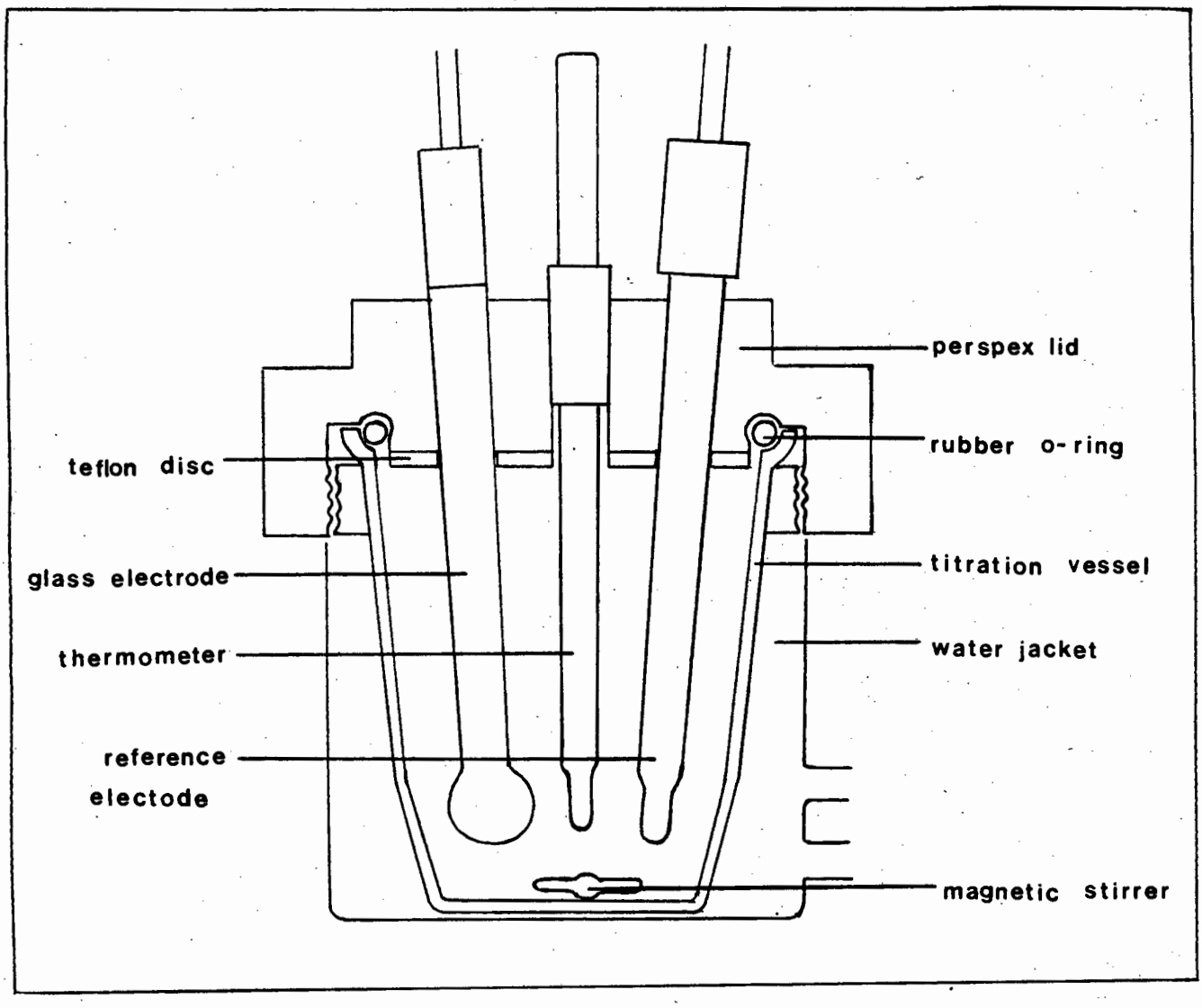


Figure A1: Diagram of the modified titration vessel used in the potentiometric study of the carbonate system.

2. Fiesser's solution for the removal of oxygen, containing 32g sodium dithionite; 1,6g sodium anthraquinone-2-sulphonate; 30g NaOH pellets in 200 ml water.

3. Distilled water.

4. Cotton wool to absorb any excess water vapour.

5. Background electrolyte, thermostatted to 25°C for vapour saturation.

Titrations were thermostatted to 25°C, the typical sequence for the potentiometric determination of the protonation constants was the following. The ligand, sodium carbonate was weighed out separately for each titration and dissolved in a solution of background electrolyte which was added from the stock solution using a manual burette to the titration vessel. The background electrolyte solution was used to make up the large volume of the ligand solution in the vessel. Sodium hydroxide was then added to raise the pH above pH 10 and the potentiometric determination of the protonation constants was carried out by titrating with the acid appropriate to the background medium. As stated in section A2, the data were analysed using the ESTA suite of programs.

A4 RESULTS AND DISCUSSION

The protonation constants have been determined in the form of overall formation constants β_{pqr}. The relationship between the overall constant and the stepwise constants used in the literature has been discussed in section A2. All concentrations are given in mol dm^{-3} unless otherwise stated.

A4.1 The protonation constants in 0.7 mol dm^{-3} sodium chloride

The value for pK_w of 13.77 relevant to 0.7 mol dm^{-3} was obtained from duplicate strong acid strong base titrations using two glass electrodes. The data was processed using MAGEC and the results are in good agreement with the values of pK_w reported by Dyrssen and Hansson [115] of pK_w 13.76 and pK_w 13.78 at 0.6 mol dm^{-3} and 0.8 mol dm^{-3} sodium chloride respectively.

The protonation constants were determined using the data from seven titrations of the ligand with hydrochloric acid between pH 11 and pH 3. Titrations were carried out at different ligand concentrations ranging between 12 x 10^{-3} mol dm^{-3} and 2 x 10^{-3} mol dm^{-3}. The ESTA2 optimization module was used to process the data, the results of which are given in table A2. The beta values determined in this study are $\log \beta_{011} = 9.66$ and $\log \beta_{012} = 15.79$.

The experimental formation curves of Z_H versus pH are presented in figure A2. Their reproducibility indicates the presence of HL and H_2L complexes only, the maximum value of Z_H being 2, which conforms to the fact that carbonic acid is diprotic. The set of betas determined were used to plot the theoretical Z_H versus pH curves presented in figure A3. These are very superimposable with the experimental plots, giving some confidence to the values determined for the betas.

Comparison of our results with those of Dyrssen and Hansson [115] show that the values obtained for the betas in this study are slightly higher than their values. Expression of their values in terms of formation constants gives the following: $\log \beta_{011} = 9.54$, $\log \beta_{012} = 15.54$. Since no other published data on the protonation constants at 0.7 mol dm^{-3} could be found for comparison with our results, it was decided to repeat the determinations at 3.0 mol dm^{-3} $NaClO_4$, the condition used by several other workers for the determination of carbonic acid protonation constants.

TABLE A2: Results of the protonation constants for carbonic acid determined in this study at 25°C

A: Protonation constants at 0.7 mol dm^{-3} sodium chloride

Complex	log β pqr	SDEV in log β
011	9.66	0.0041
012	15.79	0.0069

statistics (241 titration points)

R : 0.00655

R_{lim} : 0.00083

B: Protonation constants relevant to 3.0 mol dm^{-3} sodium perchlorate

Complex	log β pqr	SDEV in log β
011	9.56	0.0031
012	15.84	0.0055

statistics (476 titration points)

R : 0.00143

Rlim : 0.00011

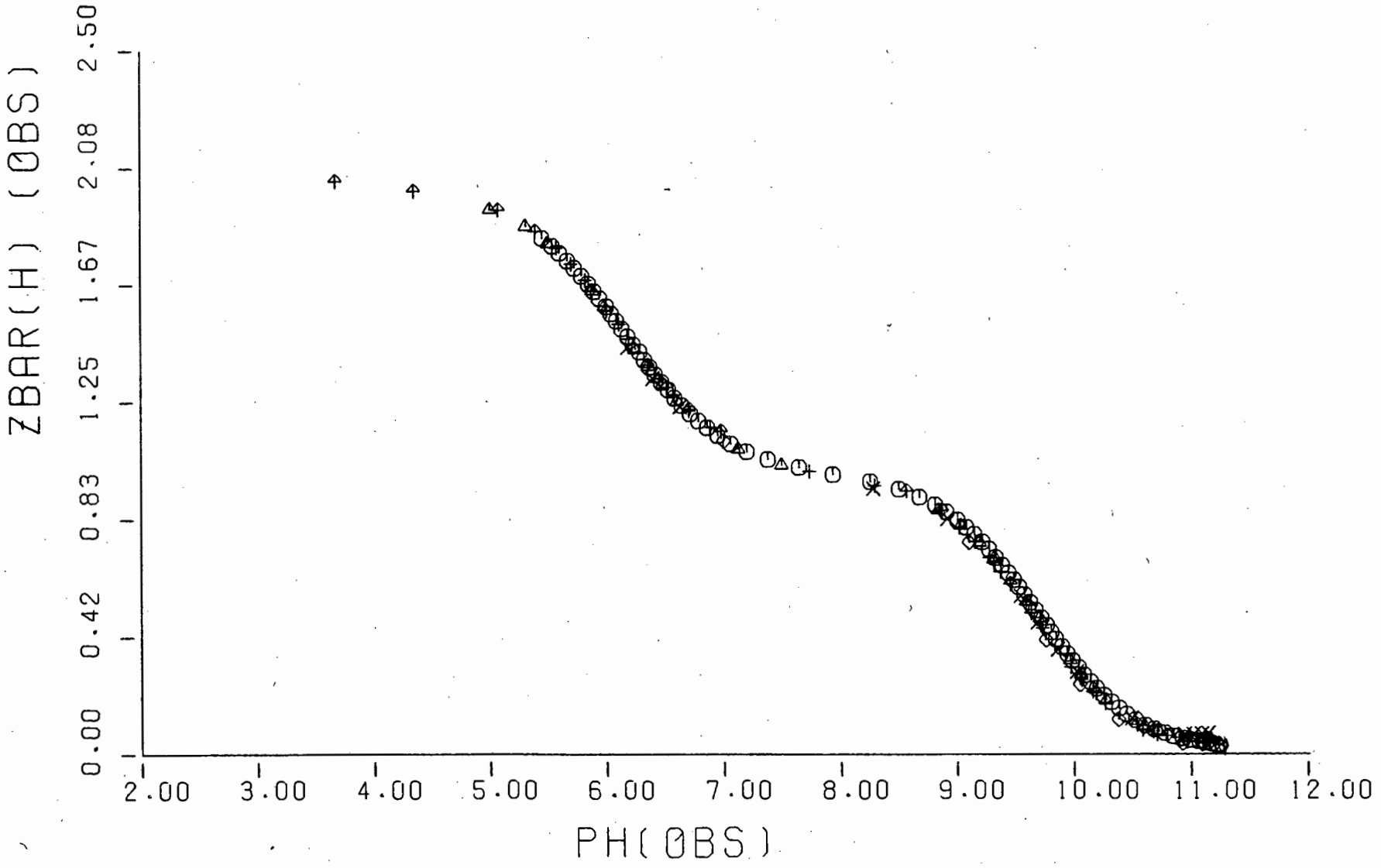


Figure A2: Experimental formation curves of Z_H versus pH for the protonation of carbonic acid at 25°C and 0.7 mol dm^{-3} sodium chloride

Once we could be sure of our technique, it was our intention to determine the formation constants for some of the important metal carbonate species at 0.7 mol dm^{-3} sodium chloride and 25°C.

A4.2 The protonation constants in 3.0 mol dm-3 sodium perchlorate

As before, strong acid strong base titrations were used to calibrate the electrodes and to obtain a value of pK_w relevant to 3.0 mol dm^{-3} $NaClO_4$. The data were analysed using the program MAGEC and a value for pK_w of 14.04 was obtained.

The protonation constants were determined using the data from our titrations (476 points) carried out between pH 11 and pH 3. Different ligand concentrations were used ranging between 12 x 10^{-3} mol dm^{-3} and 5 x 10^{-3} mol dm^{-3}. The ESTA2 optimization module was used to obtain the best set of betas, the results of which are given in table A2. The values determined for the protonation constants relevant to 3.0 mol dm^{-3} $NaClO_4$ (25°C) are $\log \beta_{011} = 9.56$ and $\log \beta_{012} = 15.84$.

The experimental formation curves of Z_H versus pH are presented in figure A4, while the theoretical curves, obtained using the computed betas are presented in figure A5. The superimposability of the two sets of curves is very good, giving some confidence to the determined betas.

The values determined by other workers are summarised in table A1. Ferri *et al* [116] determined the constant for the reaction

$$CO_2(g) + H_2O = H^+ + HCO_3^-$$

of log K = -7.987. By taking into consideration Henry's Law constant for the solubility of CO_2 relevant to 3.0 mol dm^{-3}, namely $\log K_H = -1.56$ [14], the above equilibrium can be written in terms of the aqueous phase only.

$$H_2CO_3^* = H^+ + HCO_3^-$$

with a log K value of -6.44. The protonation constant is merely the reverse of the ionization constant hence log β_{011} = 6.44. The same workers report a value for the second ionization constant of log K_2 = -9.63, taken from the data of Fryman *et al* [116]. Based on the work of Ferri et al, the value for log β_{012} is 16.07, with the result that the betas obtained in this study are slightly lower than those determined by the above authors. The recommended values for the protonation constants given in reference [38] are log β_{011} = 9.56 and log β_{012} = 15.89, which agree favourably with our values.

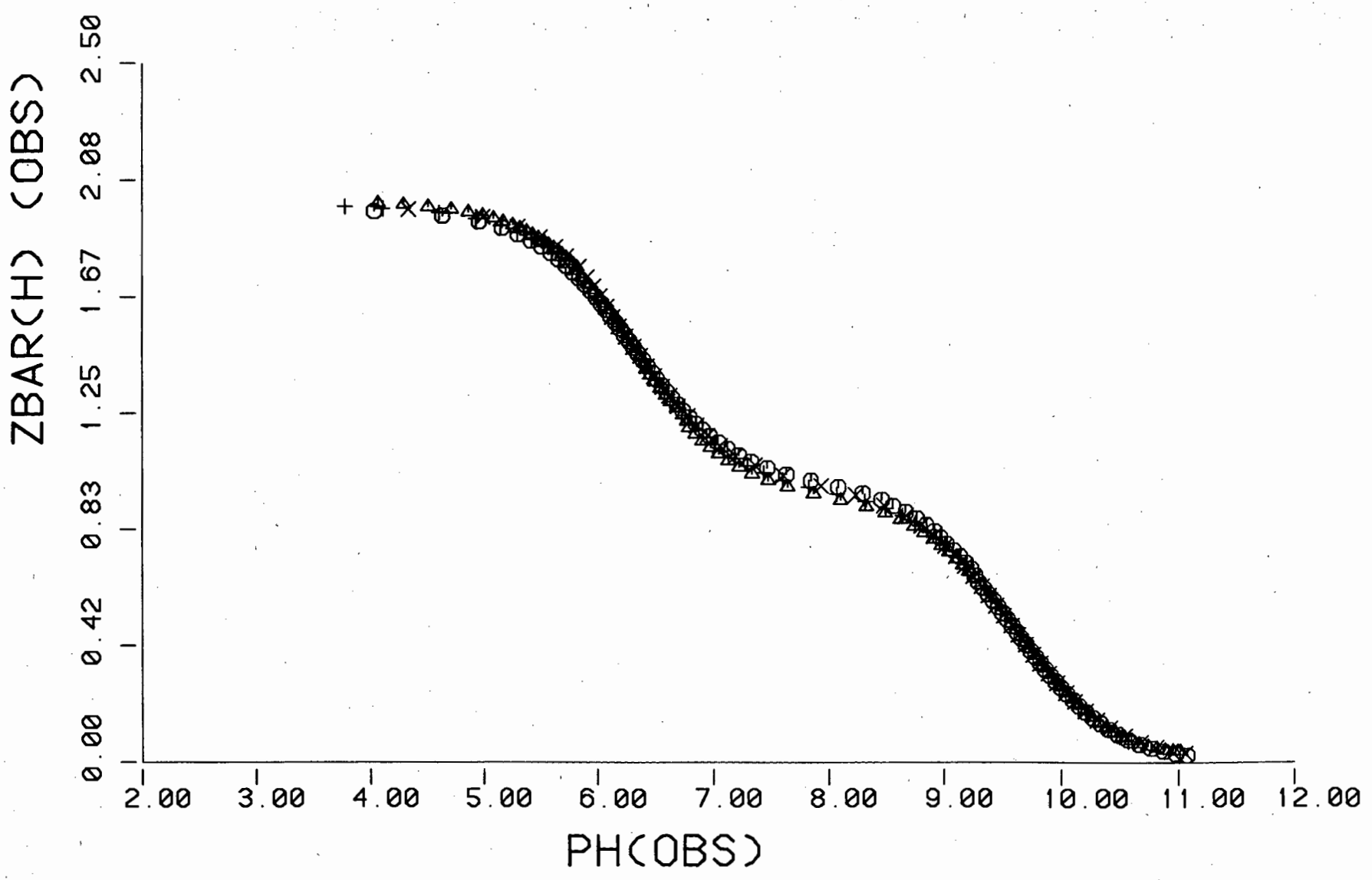


Figure A4: Experimental formation curves of Z_H versus pH for the protonation of carbonic acid at 25°C and 3.0 mol dm^{-3} sodium perchlorate

A4.3 The copper carbonate and zinc carbonate formation constants

The approach used in this study for the determination of the stability constants for the carbonate system was based on the exclusion of the gaseous phase from the reaction vessel and consideration of the aqueous phase equilibria only. Although this is not the approach chosen by most workers in this field it has the advantage that the ligand concentration remains constant throughout a titration. In keeping with this, the ligand source chosen was sodium carbonate rather than the usual CO_2 (g). This method proved successful for the determination of the protonation constants but was not successful in determining the formation constants of the carbonate anion with the metals copper and zinc. Nevertheless, it is felt that a brief discussion of our work on these systems would be of some use to other researchers involved in the determination of these formation constants.

Titrations for the determination of the copper carbonate formation constants were carried out in sodium chloride media at an ionic strength of 0.7 mol dm^{-3} and those for zinc carbonate in 3.0 mol dm^{-3} sodium perchlorate. The latter constants were determined by Ferri *et al* [127] at 3.0 mol dm^{-3} (25°C) using carbon dioxide as the ligand source. We hoped to reproduce their results using sodium carbonate as the ligand source. For the determination of the copper carbonate constants, titrations were carried out with metal to ligand rations of 1:10, 1:2 and 1:1, with total concentrations ranging between 1×10^{-3} and 1×10^{-2} mol dm^{-3}. Zinc titrations were carried out at much higher total concentrations based on the conditions used by Ferri *et al* [127]. The metal concentration was constant at 0.3 mol dm^{-3} while that of the ligand ranged between 0.01 and 0.03 mol dm^{-3}. Titrations were carried out both as acid/base titrations over a pH range and as metal titrations at a fixed pH.

Problems encountered during the course of the titrations include: the precipitation of metal hydroxide in the basic pH region above pH 6, even at ligand to metal

ratios of 10:1 and metal concentrations of 1 x 10^{-3} mol dm^{-3}; the formation of a second precipitate possibly as a result of the formation of mixed ligand species such as $Cu_2(OH)_2CO_3$ or $Cu_3(OH)_2(CO_3)_2$ in the case of copper; the appearance of bubbles of carbon dioxide on the electrodes and sides of the titration vessel below a pH of about 4. Owing to the problems of precipitate formation and ligand loss through carbon dioxide gas formation, data from acid or base titrations of the ligand solution were limited to an extremely small range of pH values. As a result it was felt that titration of the ligand solution with metal at a fixed pH between pH 5.5 and pH 6.5 may provide more useful data. An analyses of the results of the metal titrations however, showed otherwise. In this pH region approximately half of the ligand is present as the singly protonated anion, HCO_3^-, which binds metals without releasing protons. The effect of complexation on the free hydrogen ion concentration is so small because of the weakness of metal binding by the carbonate ligand, that it is difficult to measure effectively with a hydrogen ion sensitive electrode. Even the doubly charged carbonate anion is unable to compete effectively with hydroxide for the complexation of the metal.

Ferri *et al* [127] also report on the problem of precipitation which they overcome by titrating below pH 5 and over a very narrow range of pH. Since CO_2 (g) was used as their ligand source they were able to replace any ligand escaping from the system. Under these conditions the total concentration of ligand does not remain constant in the solution with a change in pH, however the concentration of the species, $H_2CO_3^*$ does.

In conclusion it would appear that the problems encountered in the metal ligand titrations were mainly due to precipitate formation and the loss of the ligand in the acidic region. Protonation titrations which could be carried out from the basic region to the acidic region were not noticeably affected by the loss of ligand as CO_2(g) below pH 4 since the bulk of the complexation data had already been

collected by that stage. In the case of the metal complexation titrations this did present a major problem since the formation of precipitates limited titrations to the pH region where $CO_2(g)$ formation occurred. In retrospect it is possible that most of the ligand had actually left the solution before the start of the titration.

Thus the experimental determinations of the first and second protonation constants of carbonic acid have been successfully concluded. The constants determined in this study at 0.7 mol dm^{-3} NaCl have been incorporated into the database set up for seawater. The determinations of the metal binding constants by the same method were not as successful, but the work done on these systems has indicated that in future studies carbon dioxide should be used as the ligand source.

APPENDIX B
THE DATABASE

Table B1: List of components and identification numbers used by MINEQL.

Id. number	component	Id. number	component
1	Ca^{2+}	34	Mn^{3+}
2	Mg^{2+}	50	protons
3	Sr^{2+}	99	electrons
4	K^{+}	101	CO_3^{2-}
5	Na^{+}	102	SO_4^{2-}
6	Fe^{3+}	103	Cl^{-}
7	Fe^{2+}	104	Fl^{-}
8	Mn^{2+}	105	Br^{-}
9	Cu^{2+}	106	I^{-}
11	Cd^{2+}	109	PO_4^{3-}
12	Zn^{2+}	110	$P_2O_7^{4-}$
13	Ni^{2+}	111	$P_3O_{10}^{5-}$
14	Hg^{2+}	112	$SiO_2(OH)_2^{2-}$
15	Pb^{2+}	116	acetylacetone
16	Co^{2+}	119	salicylate anion
17	Co^{3+}	162	phenol
18	Ag^{+}	163	propanoate anion
19	Cr^{3+}	167	3-hydroxybutyrate
20	Al^{3+}	168	acetylphenol
22	Li^{+}	169	benzoate anion
26	Sn^{2+}	170	2-hydroxy-2-methylpropionate
33	Cu^{+}		

Table B2: Listing of the database for seawater modelling constructed in this study. Constants are valid for 0.7 mol dm^{-3} and 25° C.

```
 0524
70100     2.21   1  1 101  1
70102     9.90   1  1 101  1  50  1
70104     1.03   1  1 104  1
70106   -13.09   1  1  50 -1
70108     4.26   1  1 109  1
70110    12.05   1  1 109  1  50  1
70112    18.57   1  1 109  1  50  2
70114     4.82   1  1 110  1
70116     5.60   1  1 111  1
70118    11.74   1  1 111  1  50  1
70122     1.20   1  1 102  1
70124    11.76   1  1 110  1  50  1
70126    -0.40   1  1 157  2
70128     1.11   1  1 148  1
70200     2.05   2  1 101  1
70202     9.80   2  1 101  1  50  1
70204     0.90   2  1 102  1
70206     1.32   2  1 104  1
70208   -11.50   2  1  50 -1
70209   -11.23   2  2  50 -1
70210   -54.45   2  4  50 -4
70211    13.21   2  1 109  1  50  1
70212    17.95   2  1 109  1  50  2
70213     2.62   2  1 109  1
70214     5.46   2  1 110  1
70216     7.82   2  1 110  2
70218    11.77   2  1 110  1  50 -1
70220     6.14   2  1 111  1
70222    12.20   2  1 111  1  50  1
70224     2.77   2  2 101  1
70226     0.90   2  1 148  1
70302    -4.36   3  1 101  1
70304    10.07   3  1 101  1  50  1
70306     1.29   3  1 102  1
70308     4.72   3  1 111  1
70310     6.58   3  2 111  1
70312     2.01   3  1 110  1
70314   -13.62   3  1  50 -1
70316    -0.05   3  1 157  1
70318     0.76   3  1 148  1
74000     0.30   4  1 102  1
74004     0.94   4  1 110  1
74006    11.83   4  1 109  1  50  1
74008     1.40   4  1 111  1
74010   -14.65   4  1  50 -1
74012    -0.59   4  1 106  1
74014    -0.44   4  1 157  1
75000   -14.31   5  1  50 -1
```

75004	0.63	5	1	101	1		
75006	0.33	5	1	102	1		
75008	-0.79	5	1	104	1		
75010	9.01	5	1	101	1	50	1
75012	11.79	5	1	109	1	50	1
75014	0.51	5	1	110	1		
75016	1.49	5	1	110	2		
75018	7.87	5	1	110	1	50	1
75020	1.64	5	1	111	1		
75022	9.37	5	1	111	1	50	1
75024	-0.24	5	1	148	1		
76000	2.13	6	1	102	1		
76002	2.83	6	1	102	2		
76004	0.63	6	1	103	1		
76006	0.78	6	1	103	2		
76008	-0.49	6	1	103	3		
76010	5.20	6	1	104	1		
76012	9.09	6	1	104	2		
76014	11.95	6	1	104	3		
76016	-0.20	6	1	105	1		
76018	-2.75	6	1	50	-1		
76020	-5.86	6	1	50	-2		
76022	-22.17	6	1	50	-4		
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80108     6.13    1   1 101   1
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80112   -23.22    1   1  50  -2
80114    23.68    1   3 109   2
80200     3.38    2   1 101   1
80202     3.51    2   1 101   1
80208   -18.46    2   1  50  -2
80210   -17.07    2   1  50  -2
80212    18.38    2   3 109   2
80214    15.99    2   1 109   1   50   1
83000     6.80    3   1 101   1
83002     5.10    3   1 102   1
83004     8.29    3   2 110   1
86000    23.26    6   1 109   1
86002    -3.80    6   1  50  -3
87000     9.41    7   1 101   1
87002    30.76    7   3 109   2
87004   -14.02    7   1  50  -2
88000     8.40    8   1 101   1
88002   -13.87    8   1  50  -2
88004   -42.12    8   1  50  -4   99  -2
89002     8.36    9   1 101   1
89004    15.02    9   3 101   2   50  -2
89006     4.11    9   2 101   1   50  -2
89012    -8.86    9   1  50  -2
81100    12.47   11   1 101   1
81102   -14.0    11   1  50  -2
81104   -12.39   11   1  50  -2
81202     8.73   12   1 101   1
81204   -12.80   12   1  50  -2
81206    30.18   12   3 109   2
81300     5.60   13   1 101   1
81400    27.80   14   1 106   2
81500     3.99   15   1 103   2
81502     7.24   15   1 106   2
81504    11.27   15   1 101   1
81506    21.12   15   1 109   1   50   1
81600     8.43   16   1 101   1
81602   -14.44   16   1  50  -2
81800    11.93   18   1 105   1
81802    15.77   18   1 106   1
81804     9.61   18   2 101   1
81806     3.30   18   2 102   1
82000    -9.85   20   1  50  -3
82002    51.96   20   3 112   3   50  -4    4   1
82004    40.43   20   2 112   2   50  -2
82200     2.53   22   1 104   1
82600     4.49   26   1 106   2
83300     6.44   33   1 103   1
83500    27.49   35   1 106   2
83502    15.13   35   1 101   1
83504     4.62   35   1 102   1
83506    22.28   35   1 109   1   50   1
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83508     24.54   35   3 109   2
00002
80102      6.35    1   1 101   1
81900    -12.40   19   1  50  -3
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